Laboratory Name: Ames
B&R Code: KC-02-01-01

FWP and/or subtask title under FWP:
Solidification Science

FWP Number:
AL-90-501-002

Program Scope:
This focus area has the overall objective of understanding the dynamic processes of phase selection and morphological evolution during solid-liquid phase transformations in terms of the fundamental thermodynamic and kinetic properties of the crystal-melt interface and its local response to thermal, solutal, and structural fluctuations. Efforts involve experimental and theoretical investigation a of crystal-melt interfaces under equilibrium, near equilibrium and far from equilibrium conditions. Thermodynamic and kinetic properties that ultimately govern selection dynamics are investigated over relevant length/time scales with the goal of fundamental theoretical advancement and the development of predictive capability

Major Program Achievements (over duration of support):

- We have described the structural dynamics of lamellar fault formation in regular eutectics. This involves a lateral instability in the direction normal to the lamellae, resulting in the creation of two new half-lamella or a "lamellar fault" pair which can propagate to reduce the spacing, thus governing the upper limit of the stable spacing range.
- In contrast to the existing models based on the competitive growth idea that predict a sharp transition, we found that the lamellar/rod transition in eutectics occurs dynamically and that the two morphologies can co-exist over a range of growth conditions. The transition is initiated through out-of-phase shape perturbations in adjacent lamellae, resulting in a hexagonal array of rods, and the dynamical constraint on the wavelength of perturbation was found to be critical to the condition for the transition.
- We have identified the mechanisms that lead to the strong selection of primary faceted Si bicrystalline dendritic twin-grains in directionally grown Al-Si. Our findings show that the migration of twin boundaries within the dendritic core enables efficient twin boundary reconfiguration, permitting diffusion-based evolution of sideplate structures, new primary core formation, and the selection of primary array spacing. This is a novel "hybrid" selection phenomenon where atomistic mechanisms at the growth front enable longer range diffusive optimization at the microstructural scale.
- Using in-situ XRD, EPMA, and DTA analyses, we have identified a multistage devitrification sequence in Al-Sm involving several metastable phases, including quenched-in clusters of supersaturated fcc phase which grow first during devitrification, preceding the nucleation and growth of a metastable orthorhombic $Al_{11}Sm_3$ phase.
- Using MD simulations to compare different embedded atom models for pure Al, we have found that the EA potential yields a more ordered liquid than the MSAHM potential and exhibits a critical cooling rate ($3.4 \cdot 10^{11}$ K/s) above which we observe glass formation. Given that the EA potential also yields an interfacial energy that is 1.5 time higher than the MSAHM potential, these results may suggest a critical connection between interfacial energy, liquid ordering, and glass formation tendency.

Program Impact:
The work done in this focus area is aimed at the critical unresolved fundamental issues related to selection and dynamical evolution of interface morphology and microstructure during solid-liquid phase transformations. Our emphasis on interfacial properties, growth mechanisms, and selection dynamics all address key issues that are both at the scientific forefront of the field and are also the limiting factors in the prediction and control of solidification microstructures.

Interactions:

- Internal: M.J. Kramer, C.Z. Wang, and K.M. Ho (*Correlations and Dynamics in Metallic Liquids and Associated Amorphous and Crystalline Systems*).
- External: Alain Karma (Northeastern University), Prof. J.H. Lee (Changwong National University, Korea), DOE Computational Mat. Science Network, *Impurities at interfaces*, J. Danzig (U. Illinois), M. Plapp (EP-Paris), B. Dhindaw (IIT Kharagpur).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

- R.E. Napolitano, A. Karma, W. Kurz: Organizers *"Critical Issues and Future Directions in Solidification Science,"* (A symposium in honor of Rohit Trivedi) Ames, IA, 2006.
- R.E. Napolitano, Outstanding Young Researcher, College of Engineering, Iowa State University.
- Eren Kalay, Best Student Poster and Best Photograph, 2006 MPIF Annual Meeting, San Diego, CA.
- I.E. Anderson, *2006 Iowa Inventor of the Year*
- I.E. Anderson, *2006 Fellow of American Powder Metallurgy Institute*

Personnel Commitments for FY2006 to Nearest +/- 10%:
R.E. Napolitano [Coordinator] (50%), I.E. Anderson (10%), L.S. Chumbley (10%), M.J. Kramer (10%), S. Liu (100%), M.I. Mendelev (60%), R.K. Trivedi (20%); 6 Assistant Scientists (150%); 3 Postdocs (200%); 6 Graduate Students (240%)

Authorized Budget (BA) for FY04, FY05, FY2006:
FY04 BA ~$772 k **FY05 BA** ~$1150 k **FY06 BA** ~$ 1,012k

Laboratory Name: Ames
B&R Code: KC-02-01-01

FWP and/or subtask title under FWP:
Structure of Liquid Metals

FWP Number:
AL-02-501-044

Program Scope:
The main research goal of this effort is to understand the structure and dynamics of liquid metals and alloys, both in equilibrium and in the supercooled state, in relation to the competition between (and dynamics of) crystal nucleation and glass formation. The effort ranges from accurate *ab initio* simulations of liquids, large-scale simulations of liquids and solid-liquid interfaces. Calculations of phase diagrams, non-equilibrium theory of glass formation, as well as experiments using X-ray and neutron scattering are used to examine and confirm structural and dynamical properties.

Major Program Achievements (over duration of support):
- A new EAM potential for Al has been developed and molecular dynamics simulations have been performed to study the supercooled Al liquid. Different rapid solidification behavior (i.e., crystallization vs. verification) has been observed from two different EAM Al potentials which exhibit different local order structure in the liquid state.
- Determined the self-diffusion coefficient of Cu in Al-Cu liquids using inelastic neutron scattering. Calculated values illustrate the problematic contribution of convection in conventional diffusion studies.
- Ab initio molecular dynamics simulation have been performed to study the structure of liquid Al-Cu at the eutectic composition and compared to the results from X-ray scattering.
- An accurate tight-binding potential for Ge has been developed. Tight-binding molecular dynamics has been performed to study liquid Al, Si, and Ge. Tight-binding potentials for Al-Si and Al-Ge liquid alloys are under development.
- Thermodynamic calculations have been performed to determine the T_0 curves for five simple eutectic binary alloys and for Al-rear earth (RE) alloys with intermediate compounds. The results showed that the glass forming composition of the Al-RE alloys is strongly correlated with the partitioning crystallization zone bounded by the T_0 curves, suggesting that restriction of material transport is a key factor governing the formation of glass in these systems.
- Molecular dynamics simulations have been performed to study the liquid-glass transition in a single component system (i.e., Al). The transition is determined to be first order where liquid-glass coexistence is observed for the first time.
- The phase diagram for the liquid-glass transition of a model density functional as function of the virial coefficients of the liquid has been determined by a dynamical mean field theory for self-generated glasses**.**

Program Impact:
The competition between crystal nucleation and glass formability depends on the structure, dynamics, and thermodynamic stability of a liquid alloy, yet little effort has been spent on detailed studies of these properties at the smallest length scales. The difficulty in predicting even equilibrium properties (such as phase diagrams) makes the understanding of non-equilibrium properties such as glass formability an important challenge.

Interactions:
- Contribution to theoretical efforts within scope of the Computational Materials Science Network (US DOE) project, "Fundamentals of dirty interface: from Atoms to alloy microstructures"
- *In-situ* diffraction studies at the Advanced Photon Source (Argonne National Laboratory) MU-CAT beamline.
- Large-scale computations at the National Energy Research Scientific Computing Center (NERSC)
- CNRS Laboratoire de Science et Génie des Matériaux et de Métallurgie at the Ecole des Mines de Nancy to analyse the structure of liquid and amorphous metallic alloys using neutron scattering techniques

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
- J.R. Morris and R.E. Naplitano: Organizer "*Frontiers in Solidification Science"* TMS Annual Meeting, 2005.
- J. Schmalian: Organizer, Aspen Center for Physics workshop on *Dynamics and Correlations in Glasses*, 2005; Organizer, Institute for Theoretical Physics (UCSB) Mini-workshop on *Ccomplexity in Ccorrelated Mmaterials*, 2005; Member, Science Steering Committee, Institute for Complex Adaptive Matter, Univ. of Calilfornia (2004-2005).
- D.J. Sordelet: Co-organizer, *9th International Conference on Quasicrystals* (ICQ9), 2005; Member of International Program Committee for *12th International Conference on Liquid and Amorphous Metals (LAM12)*, 2004; Member of the International Advisory Board for *International Conference on Solidification Science and Processing* (ICSSP), 2004.

Personnel Commitments for FY2006 to Nearest +/- 10%:
M.J. Kramer (10%), M.I. Mendelev (20%), J. Schmalian (10%), X. Song (10%), D.J. Sordelet (10%), C.Z. Wang (20%); 1 Assistant Scientist (10%); 2 Postdoc (140%); 2 Graduate Students (90%)

Authorized Budget (BA) for FY04, FY05, FY2006:
FY04 BA ~$415 k **FY05 BA** ~$380 k **FY06 BA** ~$336 k

Laboratory Name: Ames
B&R Code: KC-02-01-02

FWP and possible subtask under FWP:
Mechanical Behavior of Materials and Radiation Effects

FWP Number:
AL-90-501-003

Program Scope:
The research efforts in this area are concerned with understanding and comprehensively modeling the mechanical behavior of solids by elucidating the evolution, mutual interactions and collective behavior of crystalline defects from the atomistic through to the continuum scale. Integral to this effort is the use of ab initio calculations, combined with empirical methods (such as tight-binding and embedded atom model (EAM) potentials), to examine lattice stability and the nature and energy of lattice distortions, including elastic properties, phonon modes and atomistic structures of defects. In addition, three-dimensional, fully anisotropic dislocation dynamics simulations and homogenization theories are being developed and used to better elucidate the mutual interactions and collective behavior of defects over the full range of length scales. The fundamental advancements achieved from these atomistic and simulation studies are being applied to understand the electronic, physical, mechanical, and chemical factors leading to the extraordinarily high room-temperature ductility (>20% elongation) in a class of rare-earth B2 (CsCl-type) intermetallic alloys that were recently discovered at the Ames Laboratory. The critical mechanical testing experiments and subsequent metallographic studies on these new RM compounds (where R = rare earth and M = a late transition or main group metal) also serve as a source for the guidance and validation of our modeling and simulation approaches.

Major Program Achievements (over duration of support):
- Accurately simulated the role of grain size on strengthening of materials using dislocation dynamics. The structure and properties of amorphous carbon using tight-binding molecular dynamics was also accurately simulated.
- Discovered a double-period glide set dislocation structure for Si screws dislocation based on tight-binding and ab initio calculations.
- Developed accurate atomistic simulation of diffusion, coalescence, and reconstruction of vacancy defects in graphene layer.
- Single crystal slip line and TEM g·b=0 analyses revealed that <111> slip occurs in the ductile DyCu B2 intermetallic; <111> slip is unusual for B2 compounds with high ordering energies.
- By using anisotropic dislocation dynamics simulations, we were able to elucidate the unusual slip activity involving <100>{110} in RM intermetallic alloys. We also showed that, the number of dislocation configurations that form junctions is much smaller in RM intermetallic alloys in comparison to that seen in conventional intermetallics such as NiAl and Fe-25Al.

Program impact:
The studies undertaken within this effort will provide important insights into the possible dislocation reactions in highly anisotropic solids, strain-induced phase transformations, twinning-assisted slip, and grain boundary dislocation sources on the deformation behavior of polycrystalline solids in general. For instance, gaining a better understanding of the anomalously high ductility of the RM B2 intermetallics will improve our knowledge of the broader issue of deformation behavior in general solids.

Interactions:
S. Agnew (Univ. Virginia) twinning; A. Bastawros (ISU) nanoindentation; E. George (ORNL) environmental embrittlement; Y. Grin (Max Planck Inst.) electron localization function calculations. J. R. Morris ORNL. J. Li (OSU) and S. Yip (MIT) calculations and modeling of dislocation structures; Gun-Do Lee (Seoul National University, South Korea) diffusion and coalescence of vacancy defects in graphene. N. Ghooniem (UCLA) for dislocation dynamics simulations.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
S.B. Biner presented invited talks at *BES contractors meeting* in San Antonio, April 2006; and at an international conference on *Multiscale Modeling of Materials*, Freighburg Germany in September 2006. K.A. Gschneidner presented invited seminars on ductile RM intermetallics at *BES contractors meeting* in San Antonio, April 2006 and at the Max-Planck Institute for Chemical Physics of Solids, Dresden, Germany in October 2005. C. Z. Wang served as a panel member for the U. S. Department of Energy "Basic Research Needs for Advanced Nuclear Energy Systems Workshop", Bethesda, MD, July 31 – August 2, 2006.

Personnel Commitments for FY2006 to Nearest +/- 10%:
S.B. Biner (70%), K.A. Gschneidner, Jr. (10%), C.H.C. Lo (10%), M.I. Mendelev (20%), A.M. Russell (10%), C.Z. Wang (10%); 4 Assistant Scientists (30%); 2 Postdoc (140%); 4 Graduate Students (170%)

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA ~$526 k **FY05 BA** ~$505 k **FY06 BA** ~$495 k

Laboratory Name: Ames
B&R Code: KC-02-01-03

FWP and/or subtask Title under FWP:
Magnetism

FWP Number:
AL-90-501-004

Program Scope:
Research is focused on understanding the interplay between competing energy contributions in determining critical magnetic phenomena in order to formulate and validate a consistent predictive theory describing, and therefore enabling the control of magnetic phenomena at various length scales. Of particular interest are materials systems containing magnetic rare earths, transition metals, or both, where characteristic structural dimensions are on the order of the magnetic interaction lengths, or the energy difference between crystalline states is of the same order as the energy difference between magnetic states. One type of model system is a series of compounds where each member contains a well-defined structural unit of magnetic atoms while the number of atoms in this unit, and/or the arrangement of structural units varies systematically within the series. Because of periodicity, the exchange interactions between rare-earth ions in the units as well as the interactions between the units are well-defined. A second type of model system involves the controlled introduction of either growth or deformation defects into single crystals, while a third approach relies on the self-assembly of nanolayers during the eutectoid decomposition of a single crystal. In all cases, the goal is to understand and manipulate physical interactions propagating over spatial scales from atomistic to macroscopic and temporal scales that vary over several orders of magnitude.

Major Program Achievements (over duration of support):
$Pr_{(n+1)(n+2)}Ni_{n(n-1)+2}Si_{n(n+1)}$, where n = 2, 3, and 4, forms a homologous series of hexagonal compounds whose basic structural unit is a trigonal prism of Pr atoms parallel to the c-axis. The cross-section of the prism is a triangle with 3, 4, and 5 atoms on a side and 0, 1, and 3, interior atoms as n increases. Extensive phase diagram work allowed the preparation of high quality single phase polycrystalline samples and single crystals of these phases. Between 100 and 400 K, the paramagnetic moment, is close to the free-ion moment for Pr^{3+}. In all cases, the Weiss temperature, θ, is higher for H||c than for H⊥c. For H||c, $\theta_{||}$ increases with increasing *n* (the size of the prismatic column), while for H⊥c, $\theta_{\perp}$ decreases with increasing *n*. All three compounds order magnetically below 100K. For H||c the compounds exhibit ferromagnetic ordering temperatures which are in good agreement with the corresponding $\theta_{//}$ values. For H⊥c, a peak in the low-field M vs T plots appears at temperature corresponding to the values of $\theta_{\perp}$. For the three compounds at 5 K, the magnetization as a function of applied field for H||c, saturates rapidly and is weakly field dependent, as typical for ferromagnets. The saturation magnetization depends strongly on *n.* The observed values are between 25 and 50%, of the theoretical value of $g_JJ = 3.2\ \mu_B$/Pr. For H⊥c, for all three compounds, when H< 2T, dM/dH is small. Between 2 T and 3 T, for all three compounds, a metamagnetic transition is observed, while for H > 3T dM/dH is also small. This transition was studied using vector magnetization measurements. Based on the systematics of the properties of the members of the series, the magnetic properties may be understood in therms of three magnetic sites, apex, side and center. The T_c of the materials is determined by the side sites which closely couple the structural units. The saturation magnetization and the H⊥c, properties are determined by the apex sites where the magnetization is tilted at ~70° to the c axis. The component of the magnetization parallel to the c axis orders ferromagnetically with the side and center sites while the component perpendicular to the c axis orders in an incommensurate spiral at a lower temperature. For H⊥c the incommensurate spiral collapses into a canted ferromagnetic order in a field of ~2.5T.

Program Impact:
By exploiting the availability of distinct structural units varying in size from a fraction of a nanometer to several nanometers and their self-assembly of crystallographic grains ranging from a few nanometers to centimeters in size, the fundamental relationship between magnetic and structural landscapes in determining the magnetic properties of complex materials will be clarified. The ability to produce extremely high purity single crystal samples allows direct comparison with first principles calculations.

Interactions:

Internal—P. C. Canfield and B. N. Harmon (Condensed Matter Physics); G.J. Miller (Chemistry).

External— Anna Llobet Megias, LANL; Argonne and Brookhaven National Labs; Iowa State University.

Personnel Commitments for FY2006 to Nearest +/- 10%:
R.W. McCallum [Coordinator] (80%), K.A. Gschneidner, Jr. (30%), T.A. Lograsso (10%), V.K. Pecharsky (10%), J.E. Snyder (10%), X. Tan (10%); 5 Assistant Scientists (140%); 3 Postdocs (170%); 3 Graduate Students (90%)

Authorized Budget (BA) for FY04, FY05, FY2006:
FY04 BA ~$1256 k **FY05 BA** ~$1060 k F**Y06 BA** ~$1164 k

Laboratory Name: Ames
B&R Code: KC-02-01-03

FWP and possible subtask under FWP:
Extraordinary Responsive Magnetic Rare Earth Materials

FWP Number:
AL-90-501-004

Program Scope:
Coordinated experimental and theoretical investigations of the magnetic-displacive phase transformations in R_5T_4 alloys, where *R* is rare earth metal and *T* is Group 14 element – Si, Ge, Sn – or mixtures thereof, plus small substitutions of the tetravalent elements by Group 13 or Group 15 elements. The research is focused first, on the understanding of the underlying electronic structure, the microscopic and macroscopic interactions that bring about extremely strong coupling of the magnetic moments with the lattices and second, on developing and validating models of the magnetic-displacive transformation in order to facilitate future design of novel material systems exhibiting extremely large responses to small changes of magnetic field, temperature and pressure.

Major Program Achievements (over duration of support):
- Established protocols for the preparation of R_5T_4 single crystals by both Bridgman and Czochralski techniques.
- Discovered that exchange interactions and single ion-anisotropy play a major role in the stability of the R_5T_4 phases.
- Developed X-ray powder diffraction with *in situ* low temperature and high magnetic field capabilities to map the field-induced structural transformations in R_5T_4 compounds, thus linking crystallographic and physical property data.
- Discovered that the displacive, structural-only transformation in Er_5Si_4 can be affected by magnetic fields of 50 kOe or higher with the compound in the true paramagnetic state, i.e., ~200 K above its magnetic ordering temperature.
- Discovered that low-temperature, high-magnetic field, high-pressure, and high-silicon content phases near the $Gd_5Si_2Ge_2$ stoichiometry are structurally indistinguishable, thus these four different thermodynamic variables have a similar effect on the magnetic-displacive transformations in the R_5T_4 family.
- Discovered and mapped out regions where R_5T_4 compounds exist in phase separated states.
- Demonstrated that a structural change results in anisotropic magnetoresistance of $Gd_5Si_2Ge_2$ due to a significant reduction of electronic velocity in the [100] direction and the anisotropy of the electrical conductivity.
- Discovered a novel magnetic glassy state in Gd_5Ge_4.
- Discovered that Griffiths-like phase region in the paramagnetic state and short range ferromagnetic correlations in antiferromagnetic state of Gd_5Ge_4 are quenched by magnetic fields in excess of 5 kOe.
- Discovered that a structural change in Er_5Si_4 is exceptionally sensitive to pressure ($dT_t/dP = 0.03$K/bar)
- Employed exchange coupling calculations to obtain the effective Heisenberg model parameters of $Gd_5Si_2Ge_2$.
- Computed the free energy of $Gd_5Si_2Ge_2$ as a function of temperature using the mean-field approximation, reproduced a first order magneto-structural phase transition with a large value of $|\partial M/\partial T|$ which is observed experimentally.

Program Impact:
This research is being carried out by a multi-disciplinary team of researchers from the Materials and Engineering Physics, Condensed Matter Physics and Materials Chemistry Programs. A number of experimental and theoretical approaches have been brought to bear on these extraordinary R_5T_4 materials in order to understand their nature.

Interactions:

Efforts on the basic studies of magnetic-displacive phase transformations are carried out in collaboration with scientists at the US DOE Brookhaven and Argonne National Laboratories; UCLA; University of Amsterdam, the Netherlands; University of Modena, Italy; Istituto Elettrotecnico Nazionale Galileo Ferraris, Turin, Italy; University of Campinas and Rio de Janeiro, Brazil; University of Zaragosa, Spain; Centre for Advanced Technology, Indore, India; Imperial College, London, UK; and Institute of Physics of Czech Academy of Sciences, Prague, Czech Republic.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

K.A. Gschneidner, Jr. – Fellow of the American Physical Society (2002); K.A. Gschneidner, Jr. – Excellence in Research Award (MSE Department, ISU); V.K. Pecharsky – Materials Science and Engineering Department Excellence in Research Award (2003) V.K. Pecharsky – organizer of relevant sessions at international conferences (ICFE, Geneva, 2003; 20th CMD EPS, Prague, 2004, 24th Rare Earth Research Conference, Keystone, CO, 2005); V.K. Pecharsky – Distinguished Professor, Iowa State University (2006). Over 60 plenary, keynote and invited talks 2000-2006.

Personnel Commitments for FY2006 to Nearest +/- 10%:
K.A. Gschneidner, Jr. [Co-coordinator] (30%), V.K. Pecharsky [Co-coordinator] (30%), L.S. Chumbley (10%), T.A. Lograsso (20%), G.J. Miller (10%); 3 Assistant Scientists (200%); 5 Postdocs (280%); 5 Graduate Students (190%)

Authorized Budget (BA) for FY04, FY05, FY2006:
FY04 BA ~$902 k **FY05 BA** ~$1011 k **FY06 BA** ~$993 k

Laboratory Name: Ames
B&R Code: KC-02-01-03

FWP and possible subtask under FWP:
Complex Hydrides — A New Frontier for Future Energy Applications

FWP Number:
AL-04-501-051

Program Scope:
The purpose of the multidisciplinary team effort, is to achieve a fundamental understanding of the relationships between the chemical composition, bonding, structure, microstructure, properties and performance of novel hydrogen-rich solids. The specific objectives of the proposed program are to address relevant issues, which have the potential to advance basic materials science of novel hydrides and open up possibilities for their future practical use.

Major Program Achievements (over duration of support):

- Completed the acquisition of a fully automated pressure-composition-temperature apparatus to facilitate isothermal and kinetic measurements of hydrogen absorption and desorption at pressures up to 200 bar and temperatures between room temperature and 400 ºC.
- Developed a unique apparatus enabling ball-milling in hydrogen at pressures up to 300 bar H_2 in order to facilitate reversible sorption of hydrogen by materials which were difficult or impossible to hydrogenate to date.
- Designed an SEM environmental attachment enabling transfer os air-sensitive samples from a glove box to the SEM.
- Discovered that mechanochemical processing of a 1:1 (molar) mixture of $LiAlH_4$ and $LiAlNH_2$ results in a rapid release of 2/3 of the available hydrogen, yielding 6.6 wt.% hydrogen in a single step. This is the highest amount of hydrogen obtained to date from any hydrogen rich solid at room temperature.
- Developed a characterization protocol for nanocrystalline products after ball-milling. This includes solid state NMR, x-ray powder diffraction, residual pressure measurements, SEM and TEM
- Mapped out mechanisms of solid state reactions between Li(Na) amides and Li(Na) alanates. Intermediates include pure and mixed hehydroaluminates, and monohydrides of alkali metals. Final products are aluminum nitride and corresponding alkali metal monohydrides.
- Developed a series of single-tailed fluorocarbon surfactants ($F(CF_2)_{10}(CH_2)_xH$, X = 10,12,14,16,18 and $F(CF_2)_{10}(CH_2O)_4HI$), and double-tailed fluorocarbon surfactant ($F(CF_2)_8(CH_2)_2O)_2CHO(CH_2)_{16}H$) to study micelle self-assembly and facilitate controlled nanostructuring of metal hydrides.
- Discovered that the presence of a surfactant affects morphology of $Mg(AlH_4)_2$ particles prepared in situ.
- Using first principles theory discovered that the least favorable location of the doped Ti atoms in Na_3AlH_6 is Al site.
- Using available computational arsenal established that vacancies promote hydrogen desorption much better than substitutions by Ti, thus approaching a better understanding of the role of Ti dopants on hydrogenation and dehydrogenation behavior of sodium alanate and sodium hexahydroaluminate.

Program Impact:
This research is being carried out by a multidisciplinary team of scientists from the Materials and Engineering Physics and Chemical and Biological Sciences Programs in collaboration with Physics Department at Virginia Commonwealth University. A number of experimental (Ames Laboratory team) and theoretical (Virginia Commonwealth University team) approaches are brought to bear on a variety of complex metal hydrides in order not only to achieve controlled dehydrogenation, but also to achieve full rehydrogenation and long cycle life of extremely hydrogen rich solids to meet US DOE goals of volumetric and gravimetric hydrogen apacity.

Interactions:

We interact closely with P. Jena, a PI from Virginia Commonwealth University. We are also aware of activities at the DOE's Center for Excellence in Metal Hydrides at Sandia, although we have no formal collaboratiions with the Center.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

V.K. Pecharsky – Distinguished Professor, Iowa State University (2006).

Personnel Commitments for FY2006 to Nearest +/- 10%:
V.K. Pecharsky [Coordinator] (20%), L.S. Chumbley (10%), V. Lin (10%), M. Pruski (10%); 2 Postdocs (100%); 2 Graduate Students (100%)

Authorized Budget (BA) for FY05, FY2006:
FY05 BA ~$545 k **FY06 BA** ~$545 k

Laboratory Name: Ames
B&R Code: KC-02-01-05

FWP and possible subtask under FWP:
Science of Amorphous and Aperiodic Materials

FWP Number:
AL-90-501-006

Program Scope:
The primary scientific goals in this effort are directed towards gaining an increased fundamental understanding of (i) the correlation between short-range atomic order and the devitrification and deformation behavior in amorphous systems and (ii) the role of crystal chemistry (*i.e.*, composition, bonding and coordination) in controlling the structural stability of aperiodic systems. Amorphous and aperiodic structures, while nearly opposite in terms of long-range atomic order have significant interrelationships, particularly in regard to their short-range atomic order. Research efforts within this program include synthesis, structure determination and theoretical modeling studies that seek to couple pair correlation analyses with liquid and solid systems.

Major Program Achievements (over duration of support):
- Combined synchrotron X-ray diffraction data and reverse Monte Carlo simulations to model the compositional dependence of the low-Q pre-peak in the total calculated S(Q) and determine that it originates from Pt-Pt bonding.
- Obtained direct validation of *ab initio* calculations that predicted a metastable state within a narrow Zr-(Pd,Cu) composition range using high-energy X-ray diffraction
- Developed novel synthesis approach to obtain very high surface area, nano-porous monolithic foams with controlled pores sizes ranging from 10 nm to 200 μm from Ni-, Ti-, Cu- and Pt-based amorphous alloys.
- Performed MD simulations that, in agreement to experimental creep studies, show free volume is the principal mechanism responsible for homogeneous deformation behavior of metallic glasses. Moreover, high-energy X-ray diffraction data obtained from orthogonal directions revealed that free volume created during creep is anisotropic (i.e., average bond distances are larger along the loading axis than perpendicular to this direction).
- Coupled fully atomistic MD with quasi-continuum FEM simulations to illustrate that a pressure dependent yield surface, contrary to crystalline solids, develops in metallic glasses due to free volume evolution and produces a tension-compression asymmetry.

Program impact:
This effort provides critical insights into the intricate dynamics and transformation conditions affecting glass formation, non-equilibrium phase selection during devitrification, and formation of stable aperiodic and related approximant structures. Advanced high-energy X-ray scattering analysis techniques are leading to new descriptions of anisotropic free volume evolution during homogeneous deformation of metallic glasses. Collectively, these insights are also enabling the development of predictive capabilities using computational and theoretical approaches.

Interactions:
- Oak Ridge National Laboratory to perform neutron diffraction studies of Zr-Cu metallic glasses
- Advanced Photon Source at Argonne National Laboratory to perform dynamic structural investigations with high-energy X-ray scattering in time-resolved and isothermal modes
- Argonne National Laboratory, Materials and Engineering Physics Program to utilize their fluctuation electron microscopy capabilities to study medium-range order in amorphous Zr-Pd and Zr-Pt materials
- Materials Chemistry and Biomolecular Materials and Condensed Matter Physics Programs at Ames Laboratory to study surfaces and interfaces of quasicrystals as well as solute effects on metastable phase selection from metallic glasses
- Materials Chemistry and Biomolecular Materials and Condensed Matter Physics Programs at Ames Laboratory to study surfaces and interfaces of quasicrystals as well as solute effects on metastable phase selection from metallic glasses

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
M.J. Kramer, T.A. Lograsso and Y. Wu, – MRS Fall 03 Best Poster Award
D.J. Sordelet – Chair, MRS Fall 03 Quasicrystal Symposium and 9th International Conference on Quasicrystals
S.B. Biner – Chair, ECI Modeling and Simulation of Micromechanics and Microstructure Evolution 2005
M.J. Kramer – Member of Spallation Neutron Source POW-GEN3 Instrument Advisory Team
68 publications and 34 invited talks since FY2004 2003

Personnel Commitments for FY2006 to Nearest +/- 10%:
D.J. Sordelet (10%), S.B. Biner (30%), M.J. Kramer (60%), T.A. Lograsso (10%), M.I. Mendelev (10%);
6 Assistant Scientists (120%); 6 Postdocs (100%); 1 Graduate Student (50%)

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA ~$**851 k **FY05 BA ~$899 k **FY06 BA** ~$911 k

Laboratory Name: Ames
B&R Code: KC-02-01-05

FWP and possible subtask under FWP:
Materials Preparation Center

FWP Number:
AL-96-501-006

Program Scope:
The Materials Preparation Center (MPC) is a provider of exceptionally high quality research scale quantities of specialized materials and services to academic, national laboratory and industrial requesters worldwide. The unique materials synthesis and processing capabilities, which have been largely developed with Department of Energy (DOE) support of this national Specialized Single-Purpose User Facility, are made available on a full cost recovery fee basis. The MPC thus enables fundamental research and development of materials-dependent technologies by providing commercially unavailable materials and processing services. Key capabilities of the MPC include the synthesis and crystal growth of complex alloys, the processing of high-purity rare earth metals and alloys, and the synthesis of high purity metallic powders. Importantly, the MPC critically supports the Basic Energy Science (BES)-sponsored research projects within the Materials and Engineering Physics (MEP) Program at the Ames Laboratory.

Major Program Achievements (over duration of support):
- Synthesized La-Ni-Sn cryocooler alloy for the ESA/NASA Planck mission vehicle. The hydrogen storage bed materials will be used for the space-based observation vehicle, scheduled for launch in 2008.
- Established benchmarks for Al-Y-Ni-Co alloy powder purity and performance for DARPA's Structural Amorphous Materials (SAM) Program.
- Establishment of theoretical lower and upper velocity limits for stable melt-pool behavior during free-jet melt-spinning.
- Single crystals of Ti-Nb shape memory alloys have been synthesized for the first time. Ti-Nb based alloys are being considered as alternative to Ni-Ti alloys for Bio-medical applications due to their better processability, better biocompatibility, better corrosion resistance and lower modulus near the elastic modulus of human bone.
- Large single crystals of alpha-Fe-Cr-Ni alloys have been synthesized for Sandia National Laboratory researchers. These single crystals will be used to determine the mechanical properties and deformation behavior of these phase in support of a larger program on welding of stainless steels.

Program impact:
The MPC is a source and developer of unique capabilities in the preparation, purification, processing and synthesis of metals and alloys for advanced energy and technology research. In particular, the MPC enables scientific excellence by preparing research samples of significant quality and size. There is a great deal of science associated with this, to the extent that the continual need for unique material samples is, itself, one of the science drivers for the MPC. In addition, the MPC is involved via the PSI in basic science efforts directed toward the preparation of materials that are specifically germane to BES-supported projects. The MPC staff also contributes to the scientific training of students and postdoctoral researchers in the areas of materials processing and synthesis. All MPC work is non-competitive to commercial entities.

Interactions:
- D. Brown (LANL-LANSCE), F. Tang (ORNL), N. Chwala (Arizona State University): Actively-reinforced Composites
- 97 individual researchers requests for materials and services were completed in FY06, generating $409K.
- 75 Ames Laboratory researchers requested services during FY06 generating $509K of support for the MPC.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
T.A. Lograsso – Organizer, BES Workshop on Design, Discovery and Growth of Novel Materials, 2003

Personnel Commitments for FY2006 to Nearest +/- 10%:
L.L. Jones (50%), T.A. Lograsso (10%); 14 Assistant Scientists (340%); 2 Postdocs (180%)

Authorized Budget (BA) for FY04, FY05, FY06:

FY04 BA ~$**831 k **FY05 BA ~$802 k **FY06 BA ~$**854 k

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-01

FWP and possible subtask under FWP: Solid State Physics, X-ray and Neutron Scattering
MUCAT –Midwest Universities Collaborative Access Team

FWP Number: AL-90-540-001

Program Scope: The Midwest Universities Collaborative Access Team (MUCAT) was organized for the purpose of developing and operating a sector (insertion device and bending magnet lines) at the Advanced Photon Source. MUCAT saw light in the First Optics Enclosure in February 1998. Experiments on the main undulator line began late in FY99. The undulator line presently consists of two experimental stations in tandem for x-ray studies in the 3-40 keV energy range. A high-energy side station (30- 130keV), funded by FZ Juelich, allows simultaneous operations of the main line and side station. The construction of a bending magnet beam line is in progress.

This consortium brings together scientists from several universities, national and international laboratories with common interests in the use of synchrotron radiation for materials science research. The magnetic scattering and spectroscopy portion of the scientific program concentrates on resonant and nonresonant scattering studies of magnetic materials. Resonant and nonresonant magnetic x-ray scattering measurements offer important and complementary means of determining magnetic structures in materials which are ill-suited, by reasons of size or chemical composition, to traditional neutron measurements. Research efforts in the surface scattering program are centered on the study of the kinetics and growth of 2-dimensional systems, the role of defects in epitaxy, ordered non-epitaxial overlayers, phase transitions and investigations of liquid surfaces. A liquid surface diffractometer is used to probe the chemistry and physics of monolayer films at liquid surfaces. It can test and validate realistic models of biological membranes and their reaction to various stimuli and environments. High energy x-rays are used for in-situ studies of materials processing using a custom designed high temperature furnace constructed at the Ames Laboratory and for studies of pair distribution functions of poorly or partially ordered structures.

Current Capabilities:
The four-circle diffractometer and liquid surface diffractometer in 6-ID-B are well subscribed by both CAT and general users. The high-energy side station (6-ID-D) has become one of the most sought after facilities in the Sector for materials studies.

Program Impact: Publications and invited talks about MUCAT research have been growing rapidly (115 publications since 2001 including 10 Physical Review Letters, 6 Applied Physics Letters and hundreds of talks). The Sector serves a wide range of investigators both within and external to the MUCAT collaboration working in the general area of materials science. Highlights over the past year include: (1) Investigations of the influence of Quantum Size Effects on island coarsening in the Pb/Si system; (2) PDF investigations of the local atomic structure and discommensurations in the charge density wave of $CeTe_3$," and; (3) The observation of surface layering in a nonmetallic liquid.

Interactions:
Internal—Solid State Division, Alloy Behavior and Design Group, X-ray Research and Applications Group, Structural Ceramics Group.
External— Member institutions: Ames Laboratory/Iowa State, U. of Missouri, Georgia Tech, Washington U., U. of Wisconsin, Kent State, SUNY Stony Brook, Michigan State, and FZ Juelich in Germany.

Recognitions, Honors and Awards (at least in some part attributable to support under this program):
Review by APS Scientific Advisory Committee last year rated the science as "Outstanding".

Personnel Commitments for FY2006 to Nearest +/- 10%:
Douglas Robinson (100%), Jong-Woo Kim (100%), Philip Ryan (100%)

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $460k **FY05 BA $**568k **FY06 BA** $472k

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Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-01

FWP and possible subtask under FWP: Solid State Physics, X-ray and Neutron Scattering
X-ray Physics

FWP Number: AL-90-540-001

Program Scope:
The structural characterization of materials and the investigation of structural changes associated with, or leading to, novel behavior of materials. The emphasis has been on the development of techniques, such as magnetic x-ray scattering and more recently, studies of liquid structure using a novel electrostatic levitation furnace in the MUCAT sector at the APS.

Major Program Achievements (over duration of support):
The group continues to work collaboratively with B.N. Harmon's group on the origin and physics of the x-ray resonant magnetic scattering amplitudes and dichroic intensities in rare earth compounds. They have shown that the structure of antiferromagnetic domains in rare-earth compounds may be studied by resonant magnetic scattering using linearly polarized x-rays. This will have a strong impact on: (1) Investigations of compounds with proposed multiple-q structures since the scattering at each wavevector for a single domain may be studies and; (2) Complex, multicomponent magnetic systems such as rare-earth/transition metal compounds where both species carry a moment. They have also continued to develop magnetic x-ray powder diffraction measurements of rare-earth compounds using polarization analysis to separate the weak magnetic signal from the stronger charge diffuse background. This is important for preliminary measurements of complex magnetic compounds with low magnetic symmetry, presenting magnetic peaks that are difficult to locate using single crystal samples. Most recently, the group has demonstrated that investigations of ferromagnetism in rare earth compounds are possible using linearly polarized resonant magnetic scattering in the absence of an applied magnetic field. This will have an important impact upon studies of weak ferromagnetism and ferromagnets with weak anisotropy.

Program Impact:
Graduate on average one student per year, trained in x-ray scattering techniques. The magnetic scattering program is arguably one of the most productive efforts in the world, particularly in the areas of new magnetic scattering techniques, the elucidation of the origin of the resonant magnetic scattering amplitudes, and the use of magnetic scattering for *ab-initio* magnetic structure determination. In addition, together with groups from Washington University, the University of Massachusetts (Amherst) and NASA's Marshall Space Flight Center, the x-ray scattering group has had a strong impact on investigations of liquid structures using an electrostatic levitation furnace to achieve deep undercooling of liquid metals, intermetallic compounds and semiconductors.

Interactions:
Internal – Strong interactions with groups in Materials Chemistry and MEP, (e.g. the high temperature diffractometer was built with M. Kramer and R.W. McCallum (MEP)), on magnetic scattering there is strong interactions with the theory group of B. Harmon.
External – XOR (Argonne), Washington University, NASA MSFC, University of Massachusetts.

Recognitions, Honors and Awards (in some part attributable to support under this program):
Goldman is a Fellow of the American Physical Society and Director of the MUCAT (Midwest Universities Collaborative Access Team) sector at the Advance Photon Source.

Personnel Commitments for FY2006 to Nearest +/- 10%:
A. I. Goldman (PI-25%), Andreas Kreyssig (P16-50%), Students: Lizhi Tan (50%), Shibabrata Nandi (50%), Technician: Marc McGinn (25%)

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $308k **FY05 BA $**268k **FY06 BA $**449k

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-01

FWP and possible subtask under FWP: Solid State Physics, X-ray and Neutron Scattering
Neutron scattering from correlated electron materials

FWP Number: AL-90-540-001

Program Scope: A variety of neutron scattering techniques are used to study structure, dynamics, and magnetism in hard and soft matter. We explore phase transitions, lattice dynamics, magnetic structures, and magnetic excitations in exotic materials; such as superconductors, low dimensional magnetic systems, magnetostrictive and shape memory materials, ionic conductors, correlated electron systems and complex magnetic materials. We also apply reflectivity and inelastic scattering techniques to investigate thin organic films and magnetic molecules.

Major Program Achievements (over duration of support):
Inelastic neutron scattering studies of the multiferroic Li*M*PO_4 (*M* = Ni, Fe and Co) were determined and revealed unusual spin-wave anomalies in $LiNiPO_4$ that can be correlated to the unusual magnetic incommensurate structures found in this system. Magnetic excitation spectra under applied magnetic fields of the magnetic molecules $\{Cr_8\}$ and $\{Fe_{30}\}$ were determined by inelastic neutron scattering techniques and compared with theoretical predictions. Triple-axis neutron scattering experiments were performed to measure and study the spin dynamics of two compositions in a series of giant magnetostrictive Fe-Ga solid solution alloys Lattice dynamical analysis of the phonon dispersion curve data on these alloys as well as Fe-Be alloys has also begun. The program to study spin dynamics near metal-insulator transitions has been accelerated and has revealed many interesting effects related to the competition of ferromagnetic and antiferromagnetic interactions in mixed valent ferrites, Fe_3O_4, (La,Sr)FeO_3, and $YBaFe_2O_5$. These discoveries have been enabled by growing expertise in powder and single-crystal sample preparation capabilities within the group and the development of parallel algorithms for the calculation neutron scattering cross-sections of spin waves (and phonons) in complex magnetic lattices. Using the liquid surface diffractometer at the APS, a novel spectroscopy method was developed to determine ion distributions at biomimetic membranes. . The recently reinstalled and upgraded HB1A Ames Laboratory triple-axis spectrometer at the HFIR has become part of the user program at that facility. We also continue our active participation in the IDT's for the HYSPEC, SEQUOIA, and ARCS spectrometers for the newly commissioned Spallation Neutron Source (SNS), as well as in the design of CG-1 cold-neutron triple-axis spectrometer at the HFIR.

Program Impact:
Our neutron scattering findings in correlated electron oxides help understand the complex interplay between magnetism, lattice dynamics and electronic behavior. Neutron spectroscopy of magnetic molecules is crucial for testing theoretical predictions; the spectrum of $\{Mo_{72}Fe_{30}\}$ confirms theoretical predictions. Phonon and spin wave measurements in magnetoelastic materials provide valuable information needed for the microscopic understanding of the interaction of magnetic and elastic energy in these systems. Structural and magnetic studies of Li-phosphates ionic conductors help understand the effects of substitutions/vacancies on ionic conductivity, and elucidate the magneto-electric effect. The Ames Laboratory liquid surfaces diffractometer at the Advanced Photon Source has been in demand by scientists with diverse interests in materials science, biophysics, and physical chemistry,. HB1A is the one of the most reliable and heavily used instruments at the HFIR and has productivity rivaling major international triple axis instruments.

Interactions: Internal— Materials Preparation Center, numerous Ames Lab groups dealing with magnetic materials (Johnston, Canfield, Kögerler, Gschneidner, Goldman Lograsso, Schlagel, Pecharsky, Bud'ko,)
External— ORNL, BNL, LANL, NIST, Universities: California Irvine, Missouri, Johns Hopkins, Tennessee, Texas, CalTech, Purdue, Oslo (Norway), Geneva (Switzerland), Bilboa (Spain), PSI (Switzerland), ISIS (UK).

Recognitions, Honors and Awards (at least in some part attributable to support under this program)
D. Vaknin – Executive Committee, SNS and HFIR users' group. Neutron Biology Task Force.
J. L. Zarestky- Executive Committee SNS/SEQUOIA IDT, HYSPEC IDT member.
R. J. McQueeney – Executive Committee SNS/ARCS and HYSPEC. SEQUOIA IDT member.

Personnel Commitments for FY2006 to Nearest +/- 10%:
D. Vaknin (100%), J. Zarestky (90%), R. McQueeney (20%); Postdocs: Chang(100%), Li(100%), Wei(50%), Yan (100%); Students: Ma(100%), Bu(70%), Du(70%), Pratt(20%), Hamad(50%)

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $740k **FY05 BA $**912k **FY06 BA $**954k

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-02

FWP and possible subtask under FWP: Condensed Matter Physics, Experiment.
Optical Properties and Photoemission Spectroscopy of Solids and Surfaces

FWP Number: AL-90-540-002

Program Scope:
Angle-resolved photoelectron spectroscopy is used to elucidate the electronic structure and interactions in solids. Materials studied are generally metallic, and very often are systems in which electron correlations are very important. The program is developed on two parallel, but not disconnected tracks: high temperature superconductivity and heavy Fermion systems. The most pressing issues in high temperature superconductivity include investigation of the role of collective excitations, inhomogeneities, pseudogap and relation between results from various experimental techniques. The study of heavy Fermion compounds concentrates on Ce- and U-based intermetallic compounds. The new approach in this effort is to systematically study the electronic structure of families of compounds that display heavy fermion behavior. Current samples include Ce2Sb, CeSb2, USb2, RNi2B2C, RAgSb2 (R=Y, La-Nd, Sm), $Tl_2Ba_2CuO_6$, $YBa_2Cu_4O_8$. Instrumentation work includes developing a laboratory based ARPES microscope that allows studies of inhomogeneities and obtain k-resolved spectra from polycrystalline samples of novel strongly correlated materials.

Major Program Achievements (over duration of support):
The major achievements include both advances in methodology of the technique and understanding of electronic properties of specific systems: first observation (Olson, Lynch) of the superconducting gap in any cuprate by photoelectron spectroscopy (or any technique); early band mapping of two cuprates; establishment of a Fermi Surface in the cuprates; first demonstration of dispersion, hence band-like states, in a quasicrystal; showed value of using changes in energy dependent matrix elements and the cross sections to isolate details of the electronic structure; first recognition (simultaneously with IBM group) that <u>both</u> peaks in Ce compounds arise from the 4f electron; demonstration of weak dispersion in 4f bands CeSb, LaSb, Ce2Sb (via hybridization). The dispersion on one of the two Ce sites in Ce2Sb is very clear. The second site is much more localized (on one site the Ce-Ce distance is much less than in the metal, and on the other site it is greater); development of new technique – AutoCorrelated (AC) ARPES that allows direct identification of elastic and inelastic scattering processes, thus bridges the results from ARPES, STM and INS; first practical demonstration of ARPES microscopy with direct measurement of layer specific electronic structure; discovery of superconducting gap and strong renormalization effects in the quasi one dimensional chains of $YBa_2Cu_4O_8$.

Program impact:
Characterization of electronic states, often including band mapping, led to better understanding of correlation in Ce-based systems. Convinced others of importance of dipole matrix elements. Early band mapping of cuprates and observation of superconducting gap attracted wide interest. Contribution to methodology of ARPES data interpretation. ARPES microscopy holds promise to provide information about electronic structure of novel polycrystalline materials.

Interactions:
Internal: P. C. Canfield, T. Lograsso, V. Antropov, B. N. Harmon

External: J. J. Joyce (LANL), J.-S. Kang (Catholic University of Korea), Juan Carlos Campuzano (University of Illinois at Chicago), Mike Norman (Argonne National Laboratory) and Mohit Randeria (Ohio State University), Janusz Karpinski (ETH Zurich), Joel Mesot (ETH/PSI Zurich)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
82 invited talks since the inception of the photoelectron spectroscopy program. Olson and Lynch are both Fellows of the American Physical Society. Kaminski was co-organizer of workshop "Frontiers in Soft X-ray, VUV and Infrared Research" and a chairman of 38th SRC Users Meeting.

Personnel Commitments for FY2006 to Nearest +/- 10%:
D. W. Lynch (Now 0%), C. G. Olson (100%), Adam Kaminski (17%), Takeshi Kondo, Post Doc (100%)

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $300k **FY05 BA** $386k **FY06 BA** $378k

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-02

FWP and possible subtask under FWP: Solid State Physics, Experiment

FWP Number: AL-90-540-002

Program Scope:
Advanced electromagnetic measurements of novel superconducting and magnetic materials. Design and use of unconventional highly precise experimental methods in magnetism and superconductivity, including work at temperatures below 10 mK.

Major Program Achievements (over duration of support):
This new program started in July 2005. A year later "The Superconductivity and Magnetism Low-Temperature Laboratory" has become fully operational with several experiments running. In particular, a unique tunnel-diode resonator technique is currently used on a ^{3}He and ^{4}He refrigerators to study ferromagnetic and superconducting materials. This technique measures dynamic magnetic susceptibility with unprecedented sensitivity of few pico-emu (at least four orders of magnitude better than SQUID magnetometers). It is based on a self-resonating LC circuit where the measured quantity is the shift of the resonant frequency. Another unique technique already established in the lab is magneto-optical visualization of magnetic fields at surfaces. The microscope utilizes Faraday rotation in a special transparent ferrimagnetic Bi-doped iron garnet that is placed in contact with the sample. It is used to image magnetic domains in ferromagnets and flux structures in superconductors. In addition, the lab has extensive conventional experimental capabilities, including Quantum Design MPMS and PPMS systems. The MPMS has two SQUID circuits, hence capable of measuring vector magnetization, which enables direct study the effects of anisotropy. The latest addition is the large dilution refrigerator (with cooling power of 400 uW at 100 mK) installed and tested in August 2006. Current studies include pattern formation and topological hysteresis in type-I superconductors, mechanisms of superconductivity in unconventional superconductors, coexistence of superconductivity and magnetism. In a close collaboration with other groups we study critical scaling in ferromagnets (Canfield, Schmalian), magnetic defects (Johnston), magnetic molecules (Luban and Kogerler), superconducting gap structure (Kaminskii), domain structure in ferromagnets (Goldman, Kreyssig), theoretical aspects of superconductivity (Kogan, Clem), magnetic nanoparticles (bio-inspired materials program at Ames Lab).

Program impact:
Current techniques have been successfully used to study several important topics and novel materials grown by other groups. The laboratory has become an integral part of the CMP program and, as planned, provides advanced measurement capabilities to study novel effects in novel materials. With the dilution refrigerator installed, building an extensive range of experimental capabilities capable of operating at mK temperatures will be a priority for several years. The planned experiments include angle-resolved transport, AC and DC susceptometry, tunnel-diode resonator, specific heat, dilatometry, thermal conductivity, directional tunneling. This will greatly enhance the experimental capabilities of the CMP program.

Interactions: (internal) V. Antropov, S. Bud'ko, P. Canfield, J. Clem, D. Finnemore, A. Goldman, D. Johnston, A. Kaminski, V. Kogan, P. Kogerler, A. Kreyssig, M. Luban, J. Schmalian, (external) U of Illinois, U of Maryland, HMFL, Louisiana State U, U of Sherbrook, U of Tokyo (Japan), U of Bristol.

Recognitions, Honors and Awards (at least partly attributable to support under this subtask):
Sloan Research Fellowship (2006-2008)

Personnel Commitments for FY2006 to Nearest +/- 10%:
Ruslan Prozorov (PI-17%); Postdoc: A. Dobrynin (30%); graduate students: J. Hoberg (12%), R. Gordon (12%), B. McCarty (12%), M. Vannette (12%)

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA new project **FY05 BA** $158k **FY06 BA** $258k

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-02

FWP and possible subtask under FWP: Condensed Matter Physics - Experiment
Correlated states in magnetic materials – magneto-optics

FWP Number: AL-90-540-002

Program Scope:
This project was initially motivated by new capabilities for studying the optical properties of magnetic materials. With David Lynch retiring, experiments covering the low energy range of the optical spectra are made by external collaborators. This project also began with a strong experimental component for the synthesis of new materials. Paul Canfield was hired and his very successful efforts are now funded in a separate group. More recently, magnetic x-ray scattering experiments become a valuable new tool, and there are a number of collaborative projects involving the x-ray group of Alan Goldman. Materials studied are obviously magnetic. Most contain a rare earth, or a transition metal, or both. First principles electronic structure calculations are performed to understand the often-subtle MO spectra and to assess the degree and importance of correlated d- and f-electron states.

Major Program Achievements (over duration of support):
Measurement of Kerr spectra for over a dozen intermetallic compounds and successful calculation of such spectra. Observation of a metamagnetic (ferro- to antiferromagnetic) transition in $Ce(Fe_{0.9}Co_{0.1})_2$ by magneto-optic spectroscopy and MOKE spectrum in AF phase. We made the first calculations of MO spectra employing the LDA+U technique for treatment of correlated electron states (in Gd metal). The calculations were also very successful for magnetite (Fe3O4), and for a series of mixed-valent materials (Tm monochalcogenides, SmS, ThB6, etc.). Spectra were also calculated for x-ray magnetic circular dichroism (XMCD) experiments for Gd5Si2Ge2, the complex magnetic refrigeration material being investigated in Ames. We wrote a 500-page book (published in 2004 by Kluwer), presenting the techniques and results of over 20 publications in the last few years on MO and XMCD calculations. Last year we showed the simple atomic models for the L_3/L_2 intensities for rare earths (in XMCD spectra) were not correct, but full relativistic band structure calculations agreed with experiment and suggested new insights. Finally we have discovered the reason for temperature dependent changes in the XMCD spectra of Er_2Fe_{17}.

Program impact:
Systematic study of several series of compounds shows rare-earth 4f-states rarely participate directly in MOKE spectra, but their moments polarize other electrons. The off-diagonal component of the dielectric function, proportional to the magnetization, can be calculated rather accurately as long as the LDA+U technique is used to account for the strong correlations of the 4f electrons. The agreement with experiment is impressive and lends strong support for the LDA+U approach for optical spectral analysis. The success of theory in experiment in this area is excellent and we have written and published a book gathering together a large number of results. The XMCD work on rare earths is widely recognized and highly cited, and nearly unique, in that we perhaps the only group to use full band structure calculations for XMCD.

Interactions:
Internal: T. Lograsso, P. C. Canfield, A. Goldman; External: J.-Y Rhee (S. Korea), V. Antonov (Kiev)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP):
Lynch and Harmon are Fellows of the APS. 15 invited talks in last three years.
Book: "Electronic Structure and Magneto-Optical Properties of Solids" (Kluwer, end of 2004).

Personnel Commitments for FY2006 to Nearest +/- 10%:
D. W. Lynch (0%), B. Harmon (5%), V. Antropov (20%), V. Antonov (visiting scientist, Kiev, 30%), J.Y. Rhee (visiting professor, 10%), Y.B. Lee (postdoc, 30%).

Authorized Budget (BA) for FY04, FY05, FY06
FY04 BA $80k **FY05 BA** $85k **FY06 BA** $76k

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-02

FWP and possible subtask under FWP: Solid State Physics, Experimental
Correlated states in magnetic materials

FWP Number: AL-90-540-002

Program Scope:
Design, discover, grow and characterize novel materials with exotic / interesting physical properties (generally electronic / magnetic).

Major Program Achievements (over duration of support):
Over the past three fiscal years this program has been studying a wide range of intermetallic systems that manifest magnetic and / or superconducting ground states. Since January 2001 this program has been a world leader in the synthesis and characterization of MgB2, the binary intermetallic superconductor with Tc~40 K. We have delineated the mechanism of the superconductivity, range of the superconducting state and salient physical length scales, and demonstrated a simple synthetic route to making powders, wires and films. More recently (PRL 2004) carbon has been identified as a key dopant for doubling the upper critical magnetic field (from 16 T to 32 T). We also systematically studied the effects of neutron damage (PRB 2006). In addition, this program continues to be a world leader in the study of the RNi2B2C family of magnetic superconductors, the growth and properties of single grain quasicrystals (including the magnetic RMgZn family), and metamagnetic transitions and spin-glass properties in anisotropic local moment systems. During FY04 we identified YbAgGe (a member of the RAgGe family that we have been studying) as the second known, Yb-based, field induced quantum critical point compound. This discovery has generated great excitement and spawned new collaborations throughout the world (France, England, Canada, Germany, Japan). During FY06 we introduced the RT2Zn20 (T = Transition metal) series as a huge phase space for the study of correlated electron as well as local moment physics.

Program impact:
110 publications between Jan. 2004 and Nov. 2006 (as well as several patents filed on the processing of MgB2) 39 Physical Review B, 8 Physical Review Letters, as well as smaller numbers of papers in journals such as Physica C, Physica B, J. Alloys and Comp., and Journal of Magnetism and Magnetic Materials. In addition a general science review of MgB2 published in Scientific American has now been translated into over a half dozen different languages. This program's work is very highly cited. For example the work on MgB2 (less than 5 years old) has been cited over 1500 times. Given the recent nature of the research, this is a phenomenal citation rate, indicating a high impact on the field.

Interactions: (internal) A. Kaminski, R. Prozorov, V. Antropov, F. Borsa, D. Finnemore, A. Goldman, B. Harmon, V. Kogan, R. McQueeney, J. Schmalian, T. Lograsso, J. Zarestky, J. Corbett, C. Jenks, P. Thiel, M. Kramer, K. Dennis, R. McCallum, G. Miller, S. Malapragada; (external) Riso, Stanford, National High Magnetic Field Lab (LANL and Florida), ESRF (Grenoble), ILL (Grenoble), CEA (Grenoble), CNRS (Grenoble), Brookhaven National Laboratory, ISIS (England), ETH (Zurich), MPI (Dresden), as well as dozens of other labs and universities throughout the world.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Fellow of the American Physical Society (PCC); Divisional Associate Editor for Phys. Rev. Lett. (PCC), Distinguished Professor of Physics (PCC). Over 30 invited talks / colloquia, including invitations to write articles for Physics World, Physics Today, Scientific American and Encyclopedia entries on MgB_2

Personnel Commitments for FY2006 to Nearest +/- 10%:
P. Canfield (15%), S. L. Bud'ko (95%), post docs: Y. Jennsen (40%), M. Angst (10%), A. Sefat (70%), graduate students: E.D. Mun (100%), S. Jia (100%), M. Tillman (50%), N. Ni (50%), A. Thaler (30%), S. Kim (30%); undergraduate students: Stephanie Law, Josh Friedrich, David Gustafson

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $621k **FY05 BA** $740k **FY06 BA** $741k

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-02

FWP and possible subtask under FWP: Condensed Matter Physics - Experiment
Magnetic Molecules

FWP Number: AL-90-540-002

Program Scope: Broad-based experimental and theoretical research program focused on magnetism at the nano-scale level as manifested in crystalline samples of magnetic molecules. The program is a closely coordinated inter-disciplinary effort, coupling skills in synthesis chemistry and condensed matter physics so as to achieve a compre-hensive understanding of the major static and dynamic properties of molecules incorporating a finite number of exchange-coupled spin centers such as transition metal cations. The synthesis effort focuses on achieving both uncoupled and networked inorganic magnetic molecules of high symmetry. It also targets the controlled modify-cation of a wide range of parameters (symmetries, spin quantum numbers, and exchange and anisotropy parameters) to allow systematic studies of various magnetic and electronic phenomena. Experimental studies utilize thermodynamic (especially magnetization at low temperatures and high magnetic fields), magnetic resonance (NMR, EPR), optical, and neutron scattering methods. Theoretical studies utilize analytical and a wide variety of computational methods applied to classical and quantum models of magnetic molecules.

Major Program Achievements (over duration of support):
Synthesis and full chemical and physical characterization of over 60 compounds of targeted magnetic molecules comprising 2 to 30 spin centers each, and specialized preparation of compounds for experiments. Successful implementation of quantum Monte Carlo methods has added a powerful tool for developing comprehensive models of non-frustrated magnetic molecules. Development of a quantum model for the low-lying excitations of the giant Keplerate $\{Mo_{72}Fe_{30}\}$ and the intensity of inelastic neutron scattering in good agreement with experimental studies. Synthesis of $\{Mo_{72}V_{30}\}$, a spin-½ version of $\{Mo_{72}Fe_{30}\}$. Scaling law for the magnetic field and temperature dependence of the proton spin-lattice relaxation rate in magnetic molecules with antiferromagnetic exchange. Comprehensive theoretical explanation of quantum decoherence and tunneling phenomena in the $\{V_{15}\}$ system. First-principles calculation of exchange constants in polyoxovandate systems using electronic structure methods. Development of a quantitative theory of spin frustration, competing spin phases, and metamagnetic transitions in highly symmetric magnetic molecules, in some cases supporting long-lived metastable spin phases.

Program Impact:
Results of the Ames group have been published in more than 160 scientific articles on magnetic molecules between 1998-2006. This has generated scientific competition from other groups that pursue ramifications of our work as well as an increased number of collaborators in the U.S., Europe, and Asia.

Interactions:
Internal – Other CMP groups within Ames Laboratory: D. Vaknin, R. Prozorov, and D.C. Johnston.
External - *Chemical synthesis*: University of Bielefeld (Germany), University of Manchester, University of Glasgow, and University of Edinburgh (UK); *ESR and high magnetic field methods*: Tohoku University (Japan); *Optical methods*: University of Tennessee; *NMR methods*: University of Pavia (Italy), Hokkaido University (Japan), Catholic University of Korea; *Neutron facilities*: ORNL, ISIS (UK), Hahn-Meitner Institute; *Computational and Theoretical methods*: Oak Ridge National Laboratory, University of Applied Sciences-Bielefeld and University of Osnabrück (Germany), Catholic University of Nijmegen and University of Gronigen (Netherlands).

Recognitions, Honors and Awards (at least partially attributable to support under this FWP):
10-15 invited talks each year since 2001. Three articles published in *Physical Review Letters* in 2005.
M. Luban – Honorary doctorate (Dr. rer. nat. h.c.), Universität Osnabrück (Germany), 2006.

Personnel Commitments for FY2006 to Nearest +/- 10%
V. Dobrovistki (staff scientist-25%), B. Harmon (PI-5%), P. Kögerler (PI-85%), M. Luban (PI-25%); Post-doc: J. Fielden (85%); Visitors: F. Borsa, C. Schröder; Students: L. Engelhardt (50%), and I. Rousochatzakis(15%).

Authorized Budget (BA) for FY04, FY05, FY06 (project started in FY02):
FY04 BA $550k **FY05 BA** $523k **FY06 BA** $441k

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-02

FWP and possible subtask under FWP: Solid State Physics, Experimental
Photophysics of luminescent organic semiconductors and organic light-emitting diodes (OLEDs)

FWP Number: AL-90-540-002

Program Scope:
Fabrication & studies of π-conjugated thin films and OLEDs. The films are studied by photoluminescence (PL)- and PL- and photoinduced absorption (PA)-detected magnetic resonance (PLDMR and PADMR, respectively). The OLEDs are studied by current- and electroluminescence (EL)-voltage measurements, and by EL- and electrical current-detected magnetic resonance (ELDMR and EDMR, respectively).

Major Program Achievements (over duration of support):
- We have discovered conditions under which the EL spectrum of certain OLEDs is spectrally narrowed, to as little as 5 nm. We have confirmed that the emission includes both optical gain and saturation. *In other words, we have strong evidence for amplified spontaneous emission (ASE), aka mirrorless lasing, in an OLED. This is a major breakthrough in the elusive goal of achieving an organic diode laser.*
- We have completed and published, in PRL and PRB, our novel double-modulation PLDMR (DM-PLDMR) study of an archetypical derivative of poly(para-phenylene vinylene) (PPV). That study directly contradicts the "delayed PL" mechanism previously proposed to explain the PLDMR and PADMR, and its underlying assumption that the yield of singlet exitons (SE) in polymer OLEDs is >25% and may be as high as 60%. The DM-PLDMR also confirms the scenario that the central spin-dependent interaction in luminescent π-conjugated materials is the annihilation of triplet excitons (TE) by polarons. This interaction is very significant since under normal conditions the steady-state population of polarons and TEs is much higher than that of SEs. We are currently expanding this work to measure the DM-PLDMR in other π-conjugated molecules, to determine if this is the canonical behavior of luminescent p-conjugated materials.
- We are rapidly developing the new platform we invented for luminescent chemical and biological sensors and sensor arrays, in which the OLED light source is structurally integrated with the sensor film whose PL is sensitive to the target agent. We have obtained considerable funding from NASA, NSF, and NIH for practical development of this new platform.

Program impact:
Our ODMR studies support the conclusion that the maximal internal quantum efficiency of all fluorescent OLEDs is ~25%. They have also identified two PL and EL quenching mechanisms which strongly impact the EL of OLEDs at high excitation densities. Our other studies on OLEDs underpin the science for the development of organic injection lasers, OLEDs for solid-state lighting, low-cost ultrafast pulsed light-sources, and a new platform for chemical and biological sensors and microsensor arrays.

Interactions:
External – Department of Physics, Korea University; Department of Electical Engineering, MIT; Chemistry Dept, Princeton Univ; Chemistry Dept, Bowling Green State Univ; Chemistry Dept, UCLA; Appl Phys & Mat Sci Dept, City University, Hong Kong.
Local – R. Shinar & V. Dalal, Microelectr. Res. Cntr; L. Tabatabai, Biochem., Biophys., & Molec. Bio.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
27 invited talks from Oct 1, 2003 till Sept 30, 2006; 15 papers published, 1 submitted in FY06.
2004 Iowa State University Foundation Outstanding Achievement in Research Award, 2004 APS Fellow.

Personnel Commitments for FY2006 to Nearest +/- 10%:
J. Shinar, PI, 25%; Postdoctoral Fellows, 1.0 FTE; Graduate students, 4.0 FTE

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $220k **FY05 BA** $333k **FY06 BA** $318k

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-02

FWP and possible subtask under FWP: Solid State Physics – Experiment
New materials; Physical property investigations of new materials and phases

FWP Number: AL-90-540-002

Program Scope: Synthesis and study of new and improved oxide and other materials with potentially novel electronic, magnetic and/or thermal properties. Characterization of the materials using x-ray diffraction, magnetization, magnetic susceptibility, specific heat, electronic transport, thermal analysis, and NMR and NQR measurements, to understand, e.g., the electronic structure and magnetic properties of new superconductors and strongly correlated insulators and metals. Provision of high-quality single crystal and polycrystalline samples to other groups for measurements of additional properties.

Major Program Achievements (over duration of support): 1) Determined the phase relations in the Li_2O-V_2O_3-V_2O_5 ternary system at 700 ˚C for compositions in equilibrium with LiV_2O_4 and determined the temperature versus composition LiV_2O_4-Li_3VO_4 phase diagram, important for crystal growth of LiV_2O_4. 2) Carried out the first electrical resistivity, heat capacity, and magnetic susceptibility measurements on our new single crystals of the heavy fermion compound LiV_2O_4. 3) Carried out detailed ^{7}Li NMR investigations down to 0.5 K of LiV_2O_4 containing up to 0.8 mol% magnetic defects. 4) Determined the physical meanings of the two adjustable parameters in the stretched exponential relaxation function. 5) Completed studies of our new ferromagnetic oxygen defect pyrochlore structure system $Lu_2V_2O_{7-x}$ with x = 0.40–0.65. 6) Discovered that $Sr_3Cr_2O_8$ is a spin S = 1/2 spin dimer compound with a magnetic energy gap of about 35 K. 7) Completed structural, magnetization, and ^{7}Li and ^{11}B NMR studies on the spin glass compound $(Li_xV_{1-x})_3BO_5$ (x = 0.33 and 0.40). 8) Grew single crystals for the first time of the zig-zag (J_1-J_2) S = 1 chain compound CaV_2O_4. 9) Discovered long-range antiferromagnetic ordering and a structural transition in CaV_2O_4 at temperatures of 54−78 K and 110−150 K, respectively, depending on annealing conditions. 10) Discovered superconductivity in the layered boride compound OsB_2 below 2.1 K.

Program impact: Much of the progress in condensed matter physics is driven by the discovery of new or better materials. For example, our growth of LiV_2O_4 single crystals is allowing the intrinsic electronic, thermal, and magnetic properties of this unique heavy fermion material to be measured unambiguously. Our recent discovery of novel properties of magnetic defects in LiV_2O_4 also helped us maintain our lead in the area of *d*-electron heavy fermion physics. The determinations of the physical meanings of the two parameters in the ubiquitous stretched exponential relaxation function will likely have significant impact in various areas of physics, chemistry, and biology. The discovery of long-range antiferromagnetism in CaV_2O_4 is important to understanding the magnetic properties of geometrically frustrated magnetic insulators. Our discovery of superconductivity in OsB_2 is the first case of superconductivity in a boride compound containing puckered, instead of flat, boron layers.

Interactions: Internal – Ames Lab (Bud'ko, Canfield, Kaminski, Kreyssig, Schmalian, Yan)-CMP, (Kramer, Lograsso)-MEP; External-U. Hamburg, U. Tokyo, Kyoto U., U. Pavia, ETH Zürich, Catholic U. Seoul, Queen's U. (Kingston, Ontario, Canada), Hahn Meitner Inst. (Berlin, Germany), Tech. U. Braunschweig (Germany)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Fellow of the American Physical Society, 1988; Japanese Government Research Award for Foreign Specialists, 1991; Chair, Gordon Research Conference on Superconductivity, 1993; Annual Award for Outstanding Scientific Accomplishment in Solid State Physics (with 10 other Ames Lab scientists), U.S. Department of Energy, 1995; Award for Outstanding Achievement in Research, Iowa State U., 1997; Distinguished Professor, Iowa State U., 2000; named a "Highly Cited Researcher" by the Institute for Scientific Information, 2004.

Personnel Commitments for FY2006 to Nearest +/- 10%:
D. C. Johnston (group leader) 17%; A. Niazi, Y. Singh (100%, postdocs); S. Das, X. Zong (50%, graduate students).

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $181k **FY05 BA** $247k **FY06 BA $**370k

Laboratory name: Ames Laboratory
B&R Code: KC-02-02-02

FWP and possible subtask under FWP: Solid State Physics, Experiment
Control of Atomic Scale Growth on Surfaces

Program scope:
The growth of self-organized low dimensional structures is based on finding novel, robust ways to control their dimensions and geometry. If such control is achievable it would be possible to "tune" the structure electronic properties to specific technological applications. The scope of our program is to discover novel routes to this self-organization on the nanoscale. Two complementary techniques, Scanning Tunneling Microscopy (STM) and High Resolution SPA-LEED are used for structure characterization. In collaboration with theory groups worldwide we aim to attain a better understanding of the underlying growth mechanisms (i.e. diffusion, coarsening, nucleation etc.)

Major Program Achievements (over duration of support):
Identifying non-classical kinetic processes and the crucial role of the wetting layer during the growth of uniform height Pb/Si(111) islands in collaboration with the X-ray group of Miceli (Missouri) and Conrad (Georgia Tech). With CMSN (DOE supported theory network) we model the coarsening kinetics in Pb/Si(111) with a system of rate equations that includes a time dependent chemical potential for the wetting layer. With F.Liu (Utah) we have measured the nucleation site as a function of island stability (whether it is odd or even) to deduce the step edge barrier difference of ~23meV. In collaboration with the Czechs (Chvoj and Kuntova) we have constructed a non-classical potential energy surface (PES) to explain the ring like morphology during nucleation on top of the Pb islands. With SPA-LEED we have confirmed our earlier STM findings that unusually stable anisotropic Pb island growth on Si(111)-In(4x1) due to QSE are observed (for still unknown reasons) above room temperature. With STM and first-principles calculations (Ho,Wang) we have shown that the preferred separation between individual Pb atoms deposited on In(4x1) at low coverage ($\theta<0.08$ML) is an odd multiple of the Si lattice constant due to strong anti-phase interference between indirect interaction of the Pb atoms and the Charge Density Wave of the In(4x1). Since the numerous "Devil's Staircase" on Pb/Si(111)-$\alpha\sqrt{3}$x$\sqrt{3}$ phases are grown at low temperatures ~40K calculations of the collective diffusion D_c in systems with long range repulsive interactions carried out with M. Zaluska_Kotur (Polish Academy of Sciences) and Z. Gortel (University of Alberta) have shown that D_c has sharp maxima for every DS phase in agreement with the experiment.

Program Impact: Our work on the uniform height Pb islands has motivated seven other groups world wide to work on the same system and has generated over the last 5 years at least refereed 200 papers on Pb QSE-driven growth both theory and experiment. Our earlier work on surface diffusion has been recognized internationally with the invited chapter on surface diffusion included in the second edition of the classic book, *"Diffusion in Condensed Matter"* editors: J. Karger, P. Heitjans, R. Haberlandt.

Interactions: Locally: C. Z.Wang , K.-M. Ho, J.Schmalian, C. Olson, D. W. Lynch, A.Kaminski
Outside within last year with submitted papers: Ed Conrad (Georgia Tech), P, Miceli (Missouri)), Z. Chvoj (Academy of Sciences, Czech Republic), Zaluska Kotur (Polish Academy of Science) Gortel (Alberta), Argyrakis (Thessaloniki) ,F.Liu (Utah), E.Bauer (Arizona), M.Jalochowski (Lublin, Poland) **Other outside collaborators:** T.Rahman (Kansas State) Z.Zhang (Oak Ridge), J. Wendelken (Oak Ridge) M. Henzler (Hannover, Germany), M. Hon-von-Hogen (Essen Germany), K. Roos (Bradley).

Recognition:
- 2 *Physical Review Letters* and 1 *Rapid Communications* within 2006
- 13 papers published and 6 submitted within 2006
- 14 invited talks at international meetings and institutions since February 2005 co-organizer of the International Workshop on Physics and Technology of Thin Films, Prague 2006 (IWTF2) Prague June 2006. APS Fellow (2003)

Personnel Commitments for FY2006 to Nearest +/-10%:
M. C. Tringides(25%), M. Hupalo(100%), M. Yakes (50%); PhD student, J. Chen (25%)

Authorized Budget (BA) for FY04, FY05, FY06::
FY04 BA $220k **FY05 BA** $290k **FY06 BA** $318k

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-02

FWP and possible subtask under FWP: Solid State Physics, Experiment
Photonic Band Gap (PBG) Materials

FWP Number: AL-90-540-002

Program Scope:
To design, model, and fabricate novel periodic structures resulting in photonic band gap crystals.

Major Program Achievements (over duration of support):
Collaboration with Shawn Lin at Rensselaer Polytechnic Institute on thermal emission from 3D metallic photonic crystals. Economical microtransfer-molding method for fabrication of photonic crystal filaments for tailored energy-efficient thermal emitters. Experimental measurements coupling 3D PBG waveguides to resonant cavities at microwave X-band frequencies. Development of tunable infrared emitter for efficient gas sensor devices in collaboration with scientists at Ion Optics. Design of 2D PBGs for waveguides and resonant cavities. Fabrication and detailed characterization of high-quality large-scale face-centered cubic layer-by-layer structures with fundamental stop bands ranging from 1.3 to 1.7 mm using direct laser writing (*Nature Materials*). Directional emission out of a subwavelength aperture in periodically corrugated metallic thin films and PBG waveguides *(PRL).* The surface termination of PCs and the existence of surface waves were accessed. Spontaneous emission rates of dipoles in photonic crystal slabs evaluated.

Program impact:
Our group is one of the pioneers in the field of photonic crystals and continues to play a major international role in leading the development in this field. The work on metallic PBGs with exceedingly high thermal radiation may lead to very energy efficient lighting systems. Our results for emission out of subwavelength apertures hold promise for the integration of PBG waveguides with conventional optical systems.

Interactions:
Hong Kong University of Science and Technology, UC Berkeley, Rensselaer Polytechnic Institute, Canon Development America, Fudan University (China), Hanyang University (Korea), Bilkent University (Turkey), Ion Optics, Research Center of Crete, University of Twente (Netherlands), ETH, Zurich and University Karlsruhe (Germany).

Recognitions, Honors and Awards (attributable to support under this FWP or subtask):
DOE Energy 100 Award and DOE Science 100 Award, U. S. Dept. of Energy, organized three international conferences. 6 US patents have been issued to our group in this area. Soukoulis and Ho are Distinguished Professors, Iowa State Univ. and Fellows of the APS. Soukoulis is also a Fellow of AAAS and OSA, has a Senior Alexander von Humboldt Award, and is editor of the new journal *Photonics and Nanostructures: Fundamentals and Applications* since 2002.

Personnel Commitments for FY2006 to nearest +/- 10%:
Theory: K. M. Ho (15%), C. M. Soukoulis (8%), R. Biswas (50%), Postdocs: Z. Y. Li (10%), T. Koschny 20%), R. Moussa (10%); Students: A. Fang (20%), W. Dai (20%), L. Peng (20%), M. Kafesaki (unpaid), M. Li (25%).
Experiment: G. Tuttle (15%), K. Constant (9%), W. Leung (60%); postdocs: C. H. Kim (50%); students: Y-S. Kim (50%), J.-H. Lee (50%), J.Muehlmeier (50%), L. Zhang(25%), J. Zhou (25%), B. Wang (25%), H. Kang (50%)

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $591k **FY05 BA** $658k **FY06 BA** $684k

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-03

FWP and possible subtask under FWP: Condensed Matter Physics - Theory
Superconductivity Theory

FWP Number: AL-90-540-003

Program Scope:
The objective of this program is to develop theoretical understanding of the properties of superconductors in magnetic fields. We have studied the critical fields, critical currents, ac losses, and the structure and dynamics of vortices and vortex lattices. We have focused much of our attention on the effects of strong anisotropy in the high-temperature cuprate superconductors and of two-gap behavior in MgB_2.

Major Program Achievements (over duration of support):
- Introduced concepts of weak-link behavior in granular high-temperature superconductors.
- Developed theory of two-dimensional pancake vortices and interlayer Josephson vortices in layered high-temperature superconductors.
- Developed theory for the combined effects of geometrical barriers and bulk pinning on the field-dependent critical current in type-II superconducting strips.
- Wrote editorials for the *High-T_C Update* newsletter and web site.
- Using nonlocal London equations, developed theory for vortex-lattice transitions in borocarbides.
- Using a two-gap model, developed theories predicting different temperature-dependent anisotropies for the upper critical field and the London penetration depth in MgB_2.
- Developed a theory for the field dependence of the vortex-core size.

Program impact:
- New low-noise 77 K SQUIDs are currently being fabricated worldwide following our theoretical predictions that, in the earth's magnetic field, vortices are not trapped in superconducting lines of width less than ~5 μm.
- The *High-T_C Update* had a major impact on the development of high-temperature superconductivity.
- Small-angle neutron scattering, scanning tunneling microscopy, and decoration experiments in superconducting borocarbides have confirmed our predictions of vortex-lattice transitions.
- Different temperature behaviors of anisotropies of the upper critical field and of the penetration depth of MgB_2 have been confirmed in a number of experiments.

Interactions:
- Internal: P. Canfield, S. Bud'ko, D. Vaknin, R. Prozorov, and J. Schmalian
- External: Brookhaven National Lab, IBM, Los Alamos National Lab, Naval Research Laboratory, Oak Ridge National Lab, Institute of Solid State Physics (Moscow, Russia), Max Planck Institute (Germany), National Institute of Advanced Industrial Science and Technology (Japan), and these universities: Kent State, Notre Dame, Stanford, Texas A&M, Isfahan (Iran), Napoli (Italy), Tel Aviv (Israel), and Tübingen (Germany).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
- Kogan and Clem are Fellows of the American Physical Society.
- Clem: DOE Annual Award for Sustained Outstanding Research in Solid State Physics, fellow of the Institute of Physics, London, founding editor of AIP and APS's *Virtual Journal of Applications of Superconductivity,* editorial boards of *Physical Review B* and *Superconductor Science and Technology.*
- Invited talks: 302 by Clem since 1969 and 56 by Kogan since 1989.

Personnel Commitments for FY2006 to Nearest +/- 10%:
J. R. Clem (25%), V. G. Kogan (100%)

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $256k **FY05 BA** $247k **FY06 BA** $267k

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-03

FWP and possible subtask under FWP: Condensed Matter Physics - Theory
Strongly Correlated Systems

FWP Number: AL-90-540-003

Program Scope:
The development and application of modern approaches in many body theory to novel materials including hard condensed matter systems like unconventional magnets, transition metal oxides, organic conductors, heavy fermion systems, and nearly magnetic systems as well as soft condensed matter systems like micro-emulsions and physical gels formed of block-copolymers. Emphasis is given to the prediction or description of new physical effects and extreme materials properties caused by strong quantum fluctuations, the competition between interactions and disorder as well as between interactions on different length scales. Energy landscape approaches, concepts of field theory and quantum criticality and computational techniques are used.

Major Program Achievements (over duration of support):
1. Theoretical prediction for the shape and shape variations of cooperatively rearranging regions in glass forming liquids. The theory unifies seemingly contradictory results obtained in computer simulations (relevant to rather short time scales) and determined in NMR and dielectric noise experiments. It predicts a significant change of the shape of regions determining dynamical heterogeneity in glasses from stringy (at higher temperatures) to compact (at lower temperatures). 2. Theory for quantum critical Kondo volume collapse in Ce- and Yb based heavy electron systems. The theory determines the universal temperature and pressure variations of the compressibility, the thermal expansion and the heat capacity in systems with a low temperature critical end point of a volume collapse transition. Strain fluctuation induced superconductivity and non-Fermi liquid behavior are predicted where the superconducting transition temperature is enhanced compared to the weak coupling BCS expectation. 3. Development of a new theory for spin liquid behavior, superconductivity and valence bond crystal formation in the doped Mott insulator $SrCu_2(BO_3)_2$. These Quantum Monte Carlo calculations predict that the above material exhibits a strong asymmetry between electron and hole doping, yielding an insulating valence bond crystal state in one case and a strongly correlated superconductor in the other. Most interestingly, the superconducting systems undergoes a transition to an inhomogeneous checker board ordered state, which enhances superconductivity.

Program impact:
Our prediction for a new universality class in disordered quantum magnets inspired numerous NMR and neutron scattering experiments as well as many computational investigations. Our prediction for pairing in organic conductors motivated and influenced a large number of experimental efforts with very strong evidence for unconventional superconductivity. Our theory for charge Kondo superconductivity, in close collaboration with experimentalists at Stanford, initiated new experiments. Our prediction for shapes of cooperatively rearranging regions in glass-forming liquids attracted experimental as well as theoretical interest as it allows for a unified view of seemingly contradictory observations. Our theory for the quantum critical Kondo volume collapse initiated experimental investigations on field and pressure tuning of the critical end point on the volume collapse transition.

Interactions:
Internal- CMP (Tringides, Canfield, Johnston, Kogan, Kaminski, Prozorov, Ho, Harmon), Chem. (Mallapragada, Song, Lamb). External- LANL (Batista, Harris, Pines, Curro); ANL (Norman); UCSD (Wolynes), Columbia Univ. (Millis); Univ. of Wisc. (Chubukov), UIUC (Goldbart), UI-Chicago (Morr), Rutgers (Kotliar, Coleman), Univ. of Missouri (T. Vojta), Ohio State (Trivedi), Orsay (Pepin), Cologne (M. Vojta), Stanford (Fisher)

Recognitions, Honors and Awards (at least partly due to support under this FWP or subtask):
Fellow, American Physical Society (2006); Early Achievement in Research Award, ISU-Foundation (2003). Research Innovation Award of the Research Corporation (2001). 39 invited talks at major international conferences.

Personnel Commitments for FY2006 to Nearest +/- 10%:
J. Schmalian (PI-30%), D. Sheehy (postdoc, 100%), Jun Liu (student-50%)

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $140k **FY05 BA** $145k **FY06 BA** $150k

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-03

FWP and possible subtask under FWP: Condensed Matter Physics, Theory
Left –Handed Materials

FWP Number: AL-90-540-003

Program Scope:
Left-handed materials (LHMs) are composite materials with novel and unique electromagnetic (EM) properties, which are not determined by the fundamental physical properties of their constituents but by the shape and the distribution of specific patterned inclusions. The scope of the program is the theoretical understanding, analysis, development and testing of LHMs, and also the investigation of their feasibility for potential applications.

Major Program Achievements (over duration of support):
Another part of our research concerns the attempts to move the artificial magnetic response and the LH behavior from the microwaves (as in our initial experiments) to the infrared regime. We succeeded to fabricate and to demonstrate the magnetic response of Split Ring Resonator (SRR) structures operating at 6 THz (with FORTH *Opt. Lett. 30, 1348 (2005)*) and, in collaboration the University of Karlsruhe, at 100 THz (*Science 306, 1351 (2004)*) and at 200 THz *(PRL 95, 203901 (2005)*).

We design, fabricate and characterize a low-loss silver-based negative-index metamaterial. The maximum of the ratio of the real to the imaginary part of the refractive index is about three at a spectral position where Re $n = -1$. To the best of our knowledge, this is the best figure of merit reported for any negative-index photonic metamaterial to date *(Opt. Lett. 31, 1800 (2006)).* Using the same sample we were able to measure the phase and the group velocity, and found that can be both negative. These results were published in *Science 312, 892 (2006)* and have generated a lot of publicity.

Our group has been instrumental in designing new structures that give negative n with low losses and finding the limits of the highest frequency of the LHMs. (APL, 88 (221103 (2006); PRL 95, 223902 (2005); PRB 73, 041101 (2006)).

Program impact:
Provided the first transfer matrix and FDTD calculations of LHMs. Provided the first retrieval procedure to obtain the effective ε and μ of LHMs. Our work plays a major role in leading the development of LHMs both in theory and experiments.

Interactions:
External - E. Ozbay, Bilkent University, Turkey; D. R. Smith, Duke; Boeing's Phantom Works, Seattle; Research Center of Crete, FORTH; M. Wegener, Karlsruhe and J. Pendry, Imperial College.

Recognitions, Honors and Awards (at least partly attributable to support under this subtask):
Soukoulis: Distinguished Professor of Liberal Arts and Sciences, Iowa State University, 2005; shared the **Descartes award** for collaborative research on left-handed materials in 2005; Fellow of **APS**, **AAAS** and **OSA**; Senior Alexander von Humboldt Award, 2002.
Invited Talks: *Spring MRS Meeting*, San Francisco, CA, April 2006; *March Meeting of the German Physical Society,* Berlin, March 2005; *PECS-VI (**Director**)*, Crete, Greece, June 2005. Soukoulis also gave 20 additional invited talks at conferences and 8 seminars at Universities in 2005-06.

Personnel Commitments for FY2006 to nearest +/- 10%:
Soukoulis (15%), Postdoc: R. Moussa (50%), T. Koschny (40%). Visiting Sci.: E. N. Economou(10%), Peter Markos (20%); 2.5 students(100%); Unpaid associates: E. Ozbay, Jiangfeng Zhou, G. Tuttle

Authorized Budget (BA) for FY04, FY05, FY06: (New program, in FY03)
FY04 BA$145k **FY05 BA** $197k **FY06 BA** $193k

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-03

FWP and possible subtask under FWP: Condensed Matter Physics, Theory.
Dynamic Susceptibility in Magnets

FWP Number: AL-90-540-003

Program Scope: To achieve a fundamental understanding of magnetic excitations, zero-point motion and the influence of temperature dependent magnetic fluctuations in the systems with arbitrary magnetic ordering. This project is based on a new computational approach developed at Ames Laboratory and is collaboration with the group of Mark van Schilfgaarde at ASU. Some computational and methodological aspects of this project have been supported previously by DOE.

Major Program Achievements (over last 3 years):
This is a new project that received funding in late FY2006 that will be carried over to FY2007.

Program Impact:
None yet. Funding just started.

Interactions:
Collaboration exist with N.Zein (Kurchatov Institute, Moscow, Russia) magnetism theory, S.Savrasov (UC Davis) dynamic mean field theory, M.Katsnelson (Nijmegen, Netherlands) magnetism theory.
This work is being performed jointly with the group of M. van Schilfgaarde of ASU.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

Personnel Commitments for FY2006 to Nearest +/-10%:
V. Antropov (10%), Visiting Scientist (100%)

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $0k **FY05 BA $**0k **FY06 BA** $150k

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-03

FWP and possible subtask under FWP: Condensed Matter Physics, Theory
Magnetic and Electronic Properties

FWP Number: AL-90-540-003

Program Scope: This subtask is the skunkworks for condensed matter theory. It supports projects that are not restricted by specific roadmaps, and as such it has had wonderful success in spawning new initiatives such as a) Photonic Band Gap Materials, b) Magneto-Optics, which quickly evolved to Correlated States, c) Spin Dynamics, d) Mesoscale Ordering, and e) Magnetic Molecules. It was the nurturing place for the Computational Materials Science Network, and has led to funding from the Army for quantum computing simulations. Currently the subtask supports work in molecular dynamics (from first principles, to tight-binding, to classical). It supports work in disordered systems, and it supports work in bridging length scales in magnetism.

Major Program Achievements (recent):

- We found two single vacancies in a graphene layer coalesce into a 5-8-5 double vacancy at the temperature of 3000 K. It further reconstructs into a new defect structure, the 555-777 defect, by the Stone-Wales type transformation at higher temperatures. First principles calculations confirm that the 555-777 defect is energetically much more stable than two separated single vacancies, and the energy of the 555-777 defect is also slightly lower than that of the 5-8-5 double vacancy. In TBMD simulation, we found that four single vacancies reconstruct into two collective 555-777 defects which is the basic unit for the hexagonal haeckelite structure proposed by Terrones et al. This work is done in collaboration with Dr. G. D. Lee at the Seoul National University.
- We have developed a dynamical approach for understanding the properties of random lasers, especially above the laser threshold (*PRL*). When the optical gain is inhomogeneously broadened, we have recently discovered the possibility that some lasing modes are coupled through photon hopping or electron absorption and reemission, which can lead to synchronization of their lasing action for weak coupling, and to antiphase mode locking for strong coupling.
- We have developed a systematic scheme for dynamical multiscale modeling using statistical coarse graining. It allows the short wavelength modes, which are essential for thermal equilibrium, to be incorporated in models at all length scales. Successful tests of 1D and 2D systems are complete and 3D tests await a new student. A new mean field theory for treating a central spin decohereing in a bath of spins (electron in a quantum dot) has been developed, and found to be remarkably accurate.

Program Impact:
Numerous research groups have used our tight-binding potentials. The light localization and random laser work has attracted attention of several outside groups and collaborations with several research groups are exploiting the theory for new experiments and possible device designs. The multiscale modeling work has been incorporated into a micromagnetics code developed under CMSN.

Interactions:
Internal- Ames Laboratory Chemistry (K. Ruedenberg, M. Gordon, M. Schmidt)
External - J. R. Chelikowsky (U Texas, Austin); Seoul National University (Korea): Gun-Do Lee; Mingsheng Tang (China); M. Stocks (ORNL); M. Katsnelson (Nijmegen); E. Economou (Greece); and P. Markos (Slovakia).

Recognition:
The TB work was awarded the Materials Science Award for Sustained Outstanding Research in Solid State Physics (before this funding period). Ho, Soukoulis, and Harmon are APS Fellows. (As mentioned in the "scope" above, this subtask is vital for exploratory work, and has been remarkably successful.)

Personnel Commitments for FY2006 to Nearest +/- 10%:
C. Z. Wang (70%), K. M. Ho (5%), C. Soukoulis (5%), B. Harmon (5%), Three students (80%)

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $311k **FY05 BA** $228k **FY06 BA $**277k

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-03

FWP and possible subtask under FWP: Solid State Physics, Theory
Optical and Surface Physics

FWP Number: AL-90-540-003

Program Scope:
To study the structure, dynamics, and electronic properties of solid surfaces using a combination of first-principles density functional calculations and tight-binding molecular dynamics simulations. Accurate and transferable environment-dependent tight-binding (TB) potentials are developed for accurate description of surface properties as well as genetic-algorithm schemes for efficient atomistic structure optimization on surfaces.

Major Program Achievements (over duration of support):
We developed a mean-field theory to describe the unconventional and rapid coarsening observed in the Pb/Si(111) system. Quantum size effects are incorporated in the variations in chemical potentials for islands of different heights and radii. Evolution of the system is controlled by the presence of a dynamic wetting layer and the energy barriers for attachment/detachment to islands. Parameters are determined from accurate first-principles calculations. This model provides an understanding of the evolution of islands with different heights and the influence of quantum size effects and wetting layer on coarsening. The predictions of our rate equation analysis for the evolution of island density and heights distribution are in good agreement with experiments.

We used a genetic algorithm approach combined with *ab initio* calculations to determine the structure of hydrogenated <110> Si nanowires. As the number of atoms per length increases, we find that the cross section of the nanowire evolves from chains of six-atom rings to fused pairs of such chains to hexagons bounded by {001} and {111} facets. Our calculations indicate that hexagonal wires become stable starting at about 1.2 nm diameter, consistent with recent experimental reports of nanowires with diameters of about 3 nm. This work is carried out in collaboration with Prof. C. Ciobanu at the Colorado School of Mines.

Program Impact:
Our theoretical studies interact closely with experimental studies both at Ames Lab and other institutions. The interplay between the theoretical and experimental studies provides a comprehensive picture of the structures and properties of surfaces. Understanding the structures, electronic properties and dynamical behavior of surfaces and interfaces has an important impact on our ability to grow and stabilize various surface-based nanostructures such as quantum dots and quantum wires.

Interactions:
Internal- M. Tringides, M. Hupalo (Ames Laboratory-CMP), J. Evans (Ames Laboratory-Chemistry), External: C. Ciobanu (Colorado School of Mines), M. Y. Chou (Geogia Tech, Atlanta). Our group is part of a new DOE-BES Computational Materials Science Network (CMSN) project on "Formation and Stability of Surface-Based Nanostructures".

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Ho is a Fellow of the APS.
Our Tight Binding MD has been previously recognized as a DOE outstanding scientific accomplishment.

Personnel Commitments for FY2006 to Nearest +/- 10%:
C. Z. Wang (10%), K. M. Ho (5%); visiting scientists: W. Lu (30%); students: H. Wang (10%), T.-L. Chan (25%), N. Lu (50%), J. Zhang (70%)

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $98k **FY05 BA $**123k **FY06 BA $**200k

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-03

FWP and possible subtask under FWP: Condensed Matter Physics, Theory.
Spin Dynamics

FWP Number: AL-90-540-003

Program Scope: Create, develop, and use first principles methods that will allow accurate simulations at the atomistic level of complex realistic magnetic materials. We partner with ORNL scientists in implementing these methods on modern supercomputers to allow treatment of large unit cells so that thermal and other dynamical properties can be simulated. Exact quantum treatment of spin dynamics for relevant model systems is pursued.

Major Program Achievements (over last 3 years):
Achieved the first consistent explanation of the nature of hysteretic phenomena in the CoPt family of magnets. A practical synergistic combination of first principles, micromagnetic and microstructural simulations was used. We developed an approach for self-consistent calculations of the many body Green function (GW) in transition metals and insulators, and used it for *ab-initio* studies of 3d-, 4d- and 5d- metallic systems. A new general technique for the calculation of exchange coupling parameters and spin waves was developed and used for the study of numerous magnetic systems. A very accurate technique for the calculation of dynamic magnetic susceptibility and the corresponding computer codes using density functional and GW approach has been developed. Based on *ab-initio* spin dynamics simulations, we predicted the existence of large magnetic short-range order in itinerant magnets above their Curie temperature. This has the potential to radically change the common view of finite temperature magnetism and could impact many interpretations of experiments related to itinerant magnets. A new classification of magnetic materials based on this short-range order idea was proposed and applied for the real materials. A theory of spin current in non-collinear systems has been proposed and applied for Co-based multilayers. Simulation methods were developed to follow quantum spin oscillations in quantum dots and in magnetic molecules when those systems (qubits) are subjected to decoherence effects caused by a dynamical thermal spin bath of surrounding nuclear spins. An unexpected suppression of decoherence was found and explained for even numbers of qubits. Chaotic spin baths were found to be particularly effective for destroying coherence in qubit systems.

Program Impact:
Our development of first principles spin dynamics (and our treatment of non-collinear magnetism in general) has been widely disseminated, although for large systems the simulation of the thermal fluctuations in very large unit cells is still very demanding and requires considerable supercomputing resources (ORNL). Our newly proposed technique of calculation of exchange parameters is very general and is being used for both localized and itinerant magnetic systems. Our newly developed GW code is publicly available. Several experimental groups have expressed interest in pursuing our predictions of short-range magnetic order at high temperatures. The studies on spin bath decoherence are being picked up by NMR experimentalists (at Yale) to analyze recent investigations.

Interactions:
Internal – Ames Laboratory B.McCallum (MEP), R. McQueeney, and F. Borsa (CMP).
External – M. van Schilfgaarde (Arizona State), M. Stocks (ORNL), N. Zein (Russia), M. Auslander (Izrael), M. Katsnelson (Nijmegen, the Netherlands), H. De Raedt (Groningen, the Netherlands).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
This project is one of the DOE Science 100 accomplishments (for the first 25 years of DOE). Harmon is a Fellow of the American Physical Society and has helped organize focused sessions at three March meetings and the invited symposium at the MMM conference. Both Harmon and Antropov have been on the program committee of the MMM conference. Two invited review articles and 15 invited talks in last 3 years.

Personnel Commitments for FY2006 to Nearest +/-10%:
V.Antropov (PI-70%), B.Harmon (PI-5%), V. Dobrovitski (30%), Graduate student (50%), postdoc (100%).

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $421k **FY05 BA** $365k **FY06 BA** $456k
(Note: Approximately $140k/year is sent to ORNL (Stocks) as a reconciling transfer for work on this project)

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-03

FWP and possible subtask under FWP: Condensed Matter Physics, Theory.
Nuclear Spins in Nanosystems

FWP Number: AL-90-540-003

Program Scope: Development and comprehensive characterization of the novel quantum control approaches designed to mitigate the critical problem of decoherence of spins in solid-state nanostructures (electron spins in quantum dots, nuclear spins in solid-state low-dimensional systems). Determination of the optimal combination of deterministic and random protocols aiming at decoupling the system from decohering environments. Providing a detailed assessment, using both analytical and advanced numerical simulations, of performance and robustness of the developed decoupling schemes. Use of the quantum control approaches for quantum diagnostics of the experimentally relevant spin baths.

Major Program Achievements (over last 3 years):
This is a new project that received funding in late FY2006 that will be carried over to FY2007.

Program Impact:
None yet. Funding just started.

Interactions:
The work planned within this project will be performed jointly with the group of L. Viola (Dartmouth College). We will maintain close contacts and collaborate with experimental groups working on solid-state NMR device characterization and quantum metrology (Prof. D. G. Cory at MIT), and on semiconductor quantum dots (Prof. A. J. Rimberg at Dartmouth, Prof. C. Marcus at Harvard) – which will ensure direct experimental input and feedback throughout the project.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

Personnel Commitments for FY2006 to Nearest +/-10%:
V. Dobrovitski (10%), L. Viola (10%), Postdocs (100% - Dobrovitski, 50% - Viola) .

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $0k **FY05 BA $**0k **FY06 BA** $150k

Laboratory Name: Ames Laboratory
B&R Code: KC0203

FWP and/or possible subtask under FWP:
Materials Chemistry and Biomolecular Materials: 1. Electronic Stabilization in Metal-Rich Solid-State Phases

FWP Number: AL-90-360-001

Program Scope: The program seeks to expand our knowledge and understanding of solid-state chemistry by combining experiment—particularly exploratory synthesis and structure—with theory in order to uncover new families of intermetallic phases and to understand the factors that stabilize both new and known phases. These families include Zintl, cluster, Hume-Rothery, quasicrystalline, and related phases. Experiments encompass high temperature synthesis (arc melting, reactive metal fluxes, sealed metal container) and variable-temperature single crystal and powder diffraction. Theoretical efforts span first-principles to semi-empirical calculations.

Major Program Achievements (over duration of support):
We have explored, developed and organized new areas of polar intermetallics formed between active metals and the triels (Ga, In, Tl) as well as Mg, Li, Au, discovering much unique chemistry beyond the classical Zintl (valence) boundary. We synthesized and characterized new Zintl (valence) and related compounds: $K_{39}In_{80}$, K_5InPb_8, a Bergman-type structure in $Na_{11}(Cd,Tl)_{27}$, and new hyper-electronic networks ($SrIn_4$, Sr_3In_5, KAu_4In_2, $BaMg_5In_3$) with relatively low numbers of cations. We identified and interpreted electronic deviations from Zintl concepts in terms of structure, properties, and theory, i.e., the importance of atom size limitations in the stability of certain classical structure types and of electronic tuning via Li, Mg, Zn, etc. substitutions in triel networks,. New e-poorer intermetallic phases exhibiting important relativistic effects were defined for the substituted triel phases Ba_2AuTl_7, Sr_2PtTl_2, $BaAuIn_3$, and $BaAu_2In_2$. Five problem cases have been studied by ab-initio methods, demonstrating the absence of the closed shell (Zintl) anions Pb^{-4}, Bi^{-3} and Ge_2^{-6} in certain salts and the major role of sodium in the bonding in Na_3AuIn_2, Na_6TlSb_4 and KNa_3In_9. We refined a new series of binary Hume-Rothery-type intermetallics in the Zn-Pd system that provide greater insights into the stability of cubic gamma-brass structures, their relationships to quasicrystals, and some general aspects of the influence of electronic structure on complex intergrowth structures. $Zn_{1-x}Pd_x$ ($0.15 \le x \le 0.25$) were prepared (see also Bulk Structures) with six structures identified. Electronic structures show pseudogaps at the corresponding Fermi levels, with these features driven by Zn-Pd and Zn-Zn orbital interactions. Specific site preferences exist for Pd at the center of Zn-rich icosahedra, which can also be understood from theoretical calculations as well. Subsequent structural characterization of Cu–Zn gamma brasses by neutron diffraction identified a constant $[Zn_4Cu_4]$ kernel for the whole composition range. This work suggests a chemical (real space) interpretation for the stability ranges of gamma brasses.

Program Impact:
Our discoveries have impacted or motivated solid-state chemistry concepts and programs around the world and have correspondingly attracted students and visitors from many places. This impact includes groups utilizing a combination of experiment and theory to investigate problems in solid-state chemistry, as well as in thorough characterization of products beyond crystal structure determinations.

Interactions (External):
PNNL, LANL; U.S. Universities at Notre Dame, Houston, Northwestern, Michigan State, Utah State, Arizona State. Overseas organizations: Max-Planck Institutes at Stuttgart & Dresden; LGChem, Korea; FJIRSM, Fuzhou, China. Foreign Universities at Barcelona (Spain), Aachen, Cologne, Muenster & Munich (Germany), and Stockholm (Sweden).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Co-organizers, Symp. on The Chemistry of Intermetallics and Zintl Phases at 226th ACS meeting (JDC & GJM '03); National Academy of Sciences (JDC '92); two ACS National Awards in Inorganic Chemistry (JDC '86 & '00); 2 DOE Awards in Materials Chemistry (JDC '87 & '95); F. H. Spedding Award (JDC '05); Visiting Professor, ETH-Zürich (GJM '00); Visiting Scientist, MPI-CPfS Dresden (GJM '06). Total of 40 invited talks and 46 refereed publications in this subtask since 2003.

Personnel Commitments for FY2006 (Actual Effort):
J. Corbett (40%), G. Miller (5%), B. Li (100%), A. Palusyuk (100%)

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $265,000 **FY05 BA** $260,000 **FY06 BA** $260,000

Laboratory Name: Ames Laboratory
B&R Code: KC0203

FWP and/or subtask Title under FWP:
Materials Chemistry and Biomolecular Materials: 2. Bulk Structure and Structure-Property Relationships in Intermetallics and Metal-Rich Solid-State Inorganic Compounds.

FWP Number: AL-90-360-001

Program Scope: The goal is to elucidate the atomic positions in complex metal-rich solids, and in some cases to understand how this structure relates to physical properties, such as thermoelectric or magnetocaloric properties.

Major Program Achievements (over duration of support): (1) Toward quasiperiodicity in one-dimension: Exploration of the $Zn_{1-x}Pd_x$ binary system ($0.15 \le x \le 0.25$) identified a series of structures with unit cells showing two sides with common lengths and the third varying greatly, some with distances in excess of 100 Å. We could interpret these structures as intergrowths based on two different icosahedral blocks, and have developed an "algorithmic" method to prepare new structures that may lead to a one-dimensional quasiperiodic system. Four structures were solved using super-space group methods. Electron diffraction studies also show superstructures. These structures are related to the Hume-Rothery gamma-brasses, and similar behavior occurs in $Mn_{1+\delta}Ga_{1-\delta}$. (See also Electronic Stabilization) (2) Itinerant icosahedral magnets: Crystalline CrGa, MnGa, FeGa and the new compounds $Cr_xFe_{1-x}Ga$ ($0 < x < 1$) were identified, structurally characterized by X-ray and neutron diffraction, and studied for their magnetic properties. This isostructural series is a set of approximants for icosahedral quasicrystals rich in transition metals. There is a change from antiferromagnetic to ferromagnetic behavior along the binary sequence, while Cr and Fe order according to local magnetic exchange seen in MnGa. $Mn_{1+\delta}Ga_{1-\delta}$ shows formation of the cubic gamma-brass type. (3) Defect-driven distortions: Defect Heusler-type intermetallics in the Ti-Ni-Ga system show a new superstructure that creates linked icosahedra, and further establishes the relationship between bcc-type structures and icosahedral quasicrystals. Other phases in V-Co-Ga and Nb-Rh-Ga systems exist. (4) Technique Development. A technique for performing high-temperature, single crystal X-ray diffraction of air-sensitive compounds was developed and applied to study the high-temperature phase changes in $Gd_5Si_2Ge_2$ and related phases. The technique involves using silica capillaries with inserted silica rods and creating a small volume for a "getter." Using this technique we have solved numerous problems in phase transitions associated with magnetic responsive materials, $Gd_5(Si_xGe_{1-x})_4$ and $Gd_5(Ga_xGe_{1-x})_4$; (5) Phase Changes in "$Zn_{13}Sb_{10}$: $Zn_{13}Sb_{10}$ undergoes a solid-solid phase transition at 767 K and then decomposes into ZnSb and Sb before reaching its "melting temperature" of 841 K. The structure of $Zn_{13}Sb_{10}$ is characterized by disorder at many Zn sites and show two distinct phase transitions below room temperature. Characterization of its temperature-dependent physical properties corroborate the structural characterization.

Program impact: This research continues a strong tradition within the Materials Chemistry Program at the Ames Laboratory of the discovery of new metal-rich phases, the delineation of their structure, as well as their structural variation with temperature and with conditions of formation.

Interactions (External):
APS at Argonne, Los Alamos; Stanford. Overseas organizations: Max-Planck Institute at Dresden; Foreign Universities at Aachen & Munich (Germany), and Stockholm (Sweden).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Visiting Professor, ETH-Zürich (GJM '00); Co-Organizer, Symp. on The Chemistry of Intermetallics and Zintl Phases at 226th ACS meeting in New York City (GJM '03); Visiting Scientist, MPI-CPfS in Dresden (GJM '06); Symp. Co-Organizer, Quasicrystals, MRS Fall Meeting (DJS '03); Conference Co-Organizer, 9th International Conference on Quasicrystals, Ames (DJS '05); Member of International Program Committee for 12th LAM Conference (DJS '04). Total of 28 invited talks & 23 refereed papers in this topic area since 2003.

Personnel Commitments for FY2006 (Actual Effort):
G. Miller (30%), D. Shechtman (40%), M. Besser (20%), X.-F. Guo (100%), H. Ko (25%)

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $125,000 **FY05 BA $**130,000 **FY06 BA $**140,000

Laboratory Name: Ames Laboratory
B&R Code: KC0203

FWP and/or possible subtask under FWP:
Materials Chemistry and Biomolecular Materials: 3. Surface Structure and Structure-Property Relationships in Metal-Rich Solid-State Phases

FWP Number: AL-90-360-001

Program Scope: The goal is to elucidate intrinsic structural and functional aspects of surfaces of complex intermetallics, notably quasicrystals, with particular attention to the structure-property relationships. These aspects include microscopic and mesoscopic morphology, atomic locations, electronic structure, interfacial growth, friction, and chemical reactivity.

Major Program Achievements (over the last 3 years): (1) Atomic and Electronic Structure: Our work is at the forefront of understanding the nature of the clean surfaces of quasicrystals. We use various ultrahigh vacuum surface-sensitive techniques including scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), and angle-resolved low-energy ion scattering (LEIS) to probe these surfaces. By STM, we showed that temperature effects play a vital role in surface structure. A temperature change from 900 to 925 K is sufficient to dramatically alter the quasicrystal terraces; at the lower temperature, a distinctive void-rich termination is common. These results provided new insight into the way that a surface evolves toward a quasicrystalline structure. (2) Interfacial Growth: Recent work has focused on understanding the interface between crystalline and quasicrystalline materials. In particular we have examined Ag deposited on quasicrystals. We find that growth is temperature dependent. Below 300 K intrinsic trap sites dominate nucleation and thus density remains constant and 2D islands form. Above 300 K the film grows as 3D flat-topped mounds with preferred heights, thus showing quantum size effects. This may be due to the electronic pseudogap of the bulk quasicrystal, and the fact that it is present up to the surface of the quasicrystal, as we have demonstrated previously using XPS. (3) Friction and Wear: With the goal of examining the fundamental role of periodicity in friction, we realized that it is essential to measure friction under wear-free conditions. To that end, we established a collaboration with M. Salmeron and J.-Y. Park at LBNL. AFM measurements showed an 8-fold anisotropy in the friction force on a clean twofold surface of decagonal Al–Ni–Co. (The atoms are aperiodically spaced along one direction of this surface and periodically along the other.) The highest friction force was measured in the periodic direction, the lowest in the aperiodic direction, hence demonstrating that low friction forces are intrinsic to the aperiodic arrangement. This work was published in *Science* in 2005. An offshoot of this work, published in *Science* in 2006, demonstrated that free charge carriers can play a critical role in frictional energy dissipation on semiconductors.

Program Impact: Our work to date has culminated in the acceptance in the field that atomically flat quasicrystalline surfaces can be produced and that these surfaces are laterally bulk terminated; this work has implications for the relative importance of three-dimensional clusters in stabilizing the icosahedral structure. It has also demonstrated that low friction is intrinsic to the aperiodic atomic structure of a clean quasicrystalline surface, laying to rest the possibility that low friction in these materials is due (solely) to hardness or oxide chemistries. In addition, our work has motivated and facilitated many new research projects around the world.

Interactions (External):
U.S. Natl. Laboratories: LBNL, SNL-CA. U.S. Institution: Penn. State Univ. Foreign Institutions: Dalian Univ., ETH-Zürich, NIMS (Japan), CNRS-Nancy, Institut für Festköperforschung Jülich, Univ. Liverpool.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Iowa Board of Regents Award for Staff Excellence (CJ ’06); ISU P&S Council CYtation Award (CJ ’06); Co-Organizers, 9th Intl. Conf. on Quasicrystals (CJ & PT ‘05); Dr. Honoris Causa (honorary degree) from the Institut National Polytechnic de Lorraine (PT ’05), Distinguished Professor of ISU (PT ‘02); Fellow of the AVS (PT ‘01); Fellow of the APS (PT ‘01); ISU College of Liberal Arts and Sciences Award for P&S Staff Excellence (CJ ‘99); DOE Award for Outstanding Scientific Accomplishment in Materials Chemistry (CJ & PT ‘98);. Total of 18 invited talks and 32 refereed publications, including 2 in *Science* and 2 in *Physical Review Letters* from FY04 – FY06.

Personnel Commitments for FY2006:
C.J. Jenks (90%), P.A. Thiel (100%), F. Qin (50%), B. Unal (50%), D. Jing (50%), S.N. Whipple (33%)

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $380,000 **FY05 BA** $380,000 **FY06 BA** $350,000

Laboratory Name: Ames Laboratory
B&R Code: KC0203

FWP and/or possible subtask under FWP:
Materials Chemistry and Biomolecular Materials: 4. Solute Effects in Metal-Rich Solid-State Phases

FWP Number: AL-90-360-001

Program Scope: The goal is to combine experiments and theoretical calculations to elucidate the effect of small concentrations of atomic solutes on phase stability, formation pathways, and high-temperature phase transitions in solid-state inorganic materials, particularly binary glass-forming alloys. Control of low levels of solutes can be very difficult, but this is often possible for groups within the Ames Laboratory because of the specialized synthesis expertise and facilities developed here. Moreover, our time-resolved high-energy X-ray scattering techniques are especially critical for determining the dynamic evolution of glass structure and phase selection during heating.

Major Program Achievements (over the duration of support):
When a eutectic $Zr_{80}Pt_{20}$ liquid is quenched rapidly, the literature reports that an amorphous structure forms. Using special techniques to reduce O solute contents, we discovered that a bcc b-Zr(Pt) phase is formed, which is in complete contrast to the universal assumption that reducing O content increases the glass forming ability in metallic liquids. A structural model comprised of a 3x3x3 stacking of the primitive bcc b-Zr structure with Pt atoms to define superlattice positions was shown using *ab initio* calculations to be energetically favorable over other structures. In addition, experiments show that a transition to an Fd3m (Ti_2Ni-type) Zr_6Pt_3O structure occurs as the O level increases. The Ti_2Ni-type structure can accommodate oxygen in three different lattice sites. Again by using first-principles calculations, the energetic preference for oxygen atoms to fill the 16c specific Wyckoff position yielded a structural model that was consistent with the available diffraction data. More recently, studies with hyper-eutectic Zr-Pt alloys show that it is possible to obtain fully amorphous structures with oxygen contents as high as 2500 ppm mass. Time-resolved X-ray diffraction of $Zr_{71}Pt_{29}$-$Zr_{77}Pt_{23}$ glasses with varied oxygen levels shows that solute additions change the structure the as-quenched glass and influence phase selection during primary crystallization.
Among the Zintl-related polar intermetallics, we have found numerous phases that are stabilized by hydrogen or other small interstitials, especially those of the tetrels (Si–Pb) and triels (Ga–Tl) with alkaline-earth metal counterions. Many examples have Mn_5Si_3-type structures. Recent examples include Sr_5Tl_3, La_3In_{11}, and Yb_5Sn_4, all of which are actually hydrides. Many polyanionic clusters of Ga, In and Tl have been found that also take up transition metal atoms as interstitials in stoichiometric amounts, e.g., $Rb_8Tl_{11}Pd$, whereas small amounts in other clusters allow the alteration of electron counts and, therewith, stabilities.

Program Impact:
A common result is the discovery that phases reported previously in the literature were, in fact, solute-stabilized and exist only as such. It is extremely important to correct such mistakes for many reasons, among them the fact that reliable experimental data is necessary to validate high-level theory for complex solid-state systems. This is also true for metastable phases such as in the Zr-Pt system, which may well lead to a deeper understanding of the relationship between quasicrystalline and crystalline systems as well as the role of solute atoms in changing short- and medium-range order of a metallic glass and, as a consequence, the crystallization pathway.

Interactions (External):
Advanced Photon Source at ANL; US Universities at Notre Dame, Houston, Northwestern, Utah State, Arizona State. National Laboratories and Industries Overseas, at CNRS--Nancy (France), Max-Planck Institutes at Stuttgart and Dresden (Germany), LGChem (Korea), FJIRSM, Fuzhou (China). Foreign Universities at Barcelona (Spain), Cologne, Munich, Karlsruhe (Germany).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
F. H. Spedding Award in Rare Earth Research (JDC ’05); Symp. Co-Organizer, Quasicrystals, MRS Fall Meeting (DJS ‘03); Conf. Co-Organizer, 9th Intl. Conf. on Quasicrystals, Ames (DJS ‘05); Member of Intl. Program Comm. For 12th LAM Conf. and Intl. Adv. Comm. for the Intl. Conf. on Solidification Sci. & Process. (DJS ‘04). Total of 19 invited talks and 45 refereed papers since 2003.

Personnel Commitments for FY06 (Actual Effort):
D. Sordelet (50%), J. Corbett (10%), M. Kramer (10%), M. Besser (40%)

Authorized Budget (BA) for FY04, FY05, FY2006:
FY04 BA $300,000 **FY05 BA** $280,000 **FY06 BA** $305,000

Laboratory Name: Ames Laboratory
B&R Code: KC0203

FWP and/or possible subtask under FWP:
Materials Chemistry and Biomolecular Materials: 5. Macroscopic Growth of Metal-Rich Solid-State Phases

FWP Number: AL-90-360-001

Program Scope: A first goal is to design, discover, grow, and characterize novel materials with exotic and/or interesting physical properties. A second goal is to stimulate the international scientific community by sharing our high-quality samples in collaborative studies. Emphasis is placed on quasicrystalline and large-unit-cell crystalline materials. The size and quality of our samples allows the measurement of intrinsic material properties, circumventing the (oft-critical) relationship between growth quality and properties that can lead to spurious results.

Major Program Achievements (over last three years): We have been the only research group to develop synthesis routes leading to large (up to 2.5 cm^3) single grains of these binary phases, specifically the Cd–Yb icosahedral phase ($Cd_{84}Yb_{16}$), its hexagonal approximant ($Cd_{51}Yb_{14}$) and the cubic approximant ($Cd_{86}Yb_{14}$). Thus, the research group was able to study the correlations between local and long-range order in the quasicrystal phase and its corresponding approximant phase. High resolution transmission electron microcopy (HRTEM) and image simulation techniques through focal images revealed a high degree of structural perfection and the remarkable similarity between the local atomic structure of the QC and its approximant phase. This program also made single crystals of icosahedral phase ($Cd_{17}Ca_3$) and cubic approximant phase (Cd_6Ca). and the migration of pure Cd to form islands and fine whisker was investigated the role of preferential oxidation of Yb or Ca was found to be crucial for enhancing the mobility of Cd atoms across the surface. The characterization by HRTEM on these compounds is ongoing. In addition, this group is the first one to grow centimeter-sized Zn-Sc single grain approximant phase which are sufficient for neutron scattering studies. According to the prediction by M. Mihalkovic (2004) of aperiodic compounds in Mg-Ru-B, we have developed processing techniques to grow single crystals of Mg-Ru-B. Characterizations by powder XRD and single crystal diffraction showed that these single crystals do not correspond to the two known approximant phases. Further structure determination is ongoing. Evaluation of candidate low melting pure metal liquids for fluxes for the single crystal growth Ti-based quasicrystals was initiated. While an appropriate solution has yet to be found we have found and are characterizing several new ternary Ti-Zr based compounds.

Program Impact: Our efforts continue to have a significant impact on the understanding on the structure of quasicrystals and quasicrystalline surfaces and of this program has been tremendous. We continue to share high quality single crystals for collaborative research. Over 30 labs throughout the world have used the high quality quasicrystals samples synthesized at Ames Laboratory, thus allowing the field to advance at a pace faster than otherwise possible. Through such collaborations, for example, our samples have led to consensus on the fundamental surface structure of icosahedral quasicrystals.

Interactions (External): U.S. National Laboratories: ANL, BNL, LBNL, LANL, SNL; U.S. Universities at Carnegie Mellon, Penn. State, Rensselaer Polytechnic, Stanford.; National Laboratories Overseas at CNRS, INPG, ESRF, CEA, ILL, ETH-Zürich, NIMS; Foreign Universities at Banaras, Dalian, Fribourg, Liverpool, Newcastle, Nijmegen, Ottawa, Tübingen.

Recognitions, Honors and Awards (at least in some part attributable to support under this program):
MRS Fall 2003 Best Poster Award (TAL ‘03); DOE Award for Outstanding Scientific Accomplishment in Materials Chemistry (TAL & CJJ ‘98); Total of 57 refereed publications in this topic area since 2003. Note: CJJ awards listed under subtask 3.

Personnel Commitments for FY2006 (Actual Effort):
T. Lograsso (10%), C. Jenks (10%), D. Wu (50%)

Authorized Budget (BA) for FY04, FY05, FY2006:
FY04 BA $165,000 **FY05 BA** $165,000 **FY06 BA** $80,000

Laboratory Name: Ames Laboratory
B&R Code: KC0203

FWP and/or possible subtask under FWP:
Materials Chemistry and Biomolecular Materials: 6. Bioinspired Polymers: Self-assembling Hydroxyapatite-Polymer Nanocomposites

FWP Number: AL-90-360-001

Program Scope: Synthesis and characterization of novel bioinspired polymeric materials that mimic living systems in their abilities to switch among several states in response to the environment and self-assemble hierarchically. Use of these polymers as templates to direct biomineralization processes, and to facilitate a bottom-up approach to materials design. Understanding guiding mechanisms of assembly across multiple length scales through combination of experiment and theory. Advanced solid-state NMR techniques for investigating interactions of the polymeric materials with inorganic components and biomolecules.

Major Program Achievements (over duration of support): We have designed and synthesized novel bioinspired pH and temperature-sensitive block copolymers with various cationic blocks that exhibit hierarchical self-assembly from nanoscale micelles to macroscale gels and solids. Small angle neutron scattering and cryo-transmission electron microscopy studies of these polymers in solution indicate a switch from spherical to cylindrical or thread-like micelles upon increasing temperature and pH. These self-assembly processes and spherical to cylindrical transitions were also predicted by molecular dynamics simulations, where the effect of changes in temperature and pH were modeled by changing the relative hydrophobicities of the different blocks in the multiblock copolymer chains. Small angle X-ray scattering studies show that the self-assembled solids exhibit a hexagonal structure formed by the assembly of the cylindrical micelles, which is distinct from the lamellar structure seen in the melt. Different calcium phosphate phases, both hydroxyapatite and brushite, were formed on these polymer micelle templates in solution. Since the self-assembly process is driven by the relative hydrophobicities of the different polymer blocks, these nanoscale micelles coated with thin inorganic shells exhibited self-assembly into gels and solids, just as in the case of the pure polymer. New advanced solid-state NMR techniques were developed to investigate the hybrid organic-inorganic structures formed by self-assembly. These NMR techniques provide the thickness of the inorganic layer formed (of the order of a few nm) as well as compositional information about the nanoscale inorganic layer at the organic-inorganic interface, which is very difficult to obtain using other established techniques. In addition, small angle X-ray scattering studies of these hybrid gels and solids at Argonne indicated that the hexagonal structure of the polymer gels was preserved even in the presence of the inorganic coatings on the micelles and did not alter the self-assembly process of the underlying polymer template. The chemical structure of the polymer template was seen to have a significant role on the mineralization process and the thickness and composition of the calcium phosphate layer formed.

Program Impact:
Self-assembly across multiple length scales is key to the development of a “bottom-up” approach to materials design and our research has generated a new class of hierarchically self-assembled nanocomposites. We have developed NMR techniques that are being used worldwide by other groups.

Interactions:
Argonne National Laboratory; Univ. of Paris, EPFL; Technion, Israel; Koc University, Turkey.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
NSF-CAREER award (SKM, ‘00); MIT's Technology Review’s "Top 100 Young Innovators" list (SKM, ‘02); John H. Dillon Medal of the American Physical Society (KSR-‘01); Fellow of AIMBE (SKM, ’06), Ross Coffin Purdy Award (MAA, ’06) 20 refereed publications and 22 invited talks since 2003.

Personnel Commitments for FY2006 (Actual Effort):
S.K. Mallapragada (20%), M. Determan (50%), A. Agarwal (50%), A. Travesset-Casas (10%), J. Anderson (5%), K. Schmidt-Rohr (5%), A. Rawal (5%), M.A. Akinc (10%), X. Wei (50%), D. Enlow (50%)

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $245,000 **FY05 BA** $245,000 **FY06 BA** $240,000

Laboratory Name: Ames Laboratory
B&R Code: KC0203

FWP and/or subtask Title under FWP:
Materials Chemistry and Biomolecular Materials: 7. NMR Technique Development

FWP Number: AL-90-360-001

Program Scope: Development and application of advanced solid-state nuclear magnetic resonance (NMR) methods and scattering simulations for elucidating the nanometer-scale structure and dynamics of heterogeneous polymer-based materials under the following types of conditions: Ionomers as used, for instance, in all-solid H_2/O_2 fuel cells; Biological and biomimetic apatite-polymer nanocomposites; Polymers intercalated in layered silicates.

Major Program Achievements (over duration of support):

Structure of Nafion: A definitive new model of the nanometer-scale structure of the Nafion ionomer, used in fuel-cell proton-exchange membranes, has been developed based on NMR and quantitative scattering analysis. High-resolution ^{13}C NMR of fluorinated polymers such as Nafion and PTFE (Teflon) was achieved for the first time, by fast magic-angle spinning and pulsed ^{19}F decoupling; it revealed a high degree of conformational order of the Teflo-like backbone of Nafion. Advanced NMR experiments show that Nafion backbones form rotating, conformationally ordered helices that pack with limited orientational order. The branch points are relatively immobile, while the anionic sidegroups move significantly in the presence of water. In order to characterize the supramolecular structure, we have developed an algorithm for simulating small-angle scattering data using multidimensional numerical Fourier transformation as familiar from 2D NMR. On this basis, we can exclude all specific models of Nafion previously proposed; we prove that instead of spherical clusters, bilayers, or polymer bundles, the ionic sidegroups form long, parallel water channels of ~ 2.5 nm diameters, which explain the salient properties of Nafion.

Structure of Biological and Biomimetic Nanocomposites: The apatite-collagen nanocomposite in bone has been elucidated in terms of the composition of both components and their distances from the organic-inorganic interface. Several new NMR approaches for studying nanocomposites, including HeteronucleAr Recoupling with Dephasing by Strong Homonuclear Interactions of Protons (HARDSHIP), have been introduced. They have revealed the thickness of apatite nanocrystals in bone, the concentration and location of carbonate and hydroxide ions, the presence of bound and viscous water layers at the interface, and the COO^- and CH-OH apatite-binding sites of collagen. These methods have then been applied to biomimetic polymer-apatite nanocomposites.

Improved Characterization of Heterogeneous Polymers: New ^1H spin diffusion NMR methods for characterizing heterogeneities in multicomponent polymer materials, on the 0.5 - 50 nm scale, have been introduced. They provide improved contrast through ^{13}C evolution and detection, and improved accuracy by calibration of local spin diffusion coefficients. Sensitivity enhancement (4 - 10-fold) has been achieved in various NMR experiments by indirect ^1H detection, signal refocusing, or multiple alternating depolarization.

Heterogeneous para/ferromagnetic polymer materials. Many polymer-based materials contain para- or ferromagnetic particles. New insights into their effects on the NMR of the polymer matrix have been obtained.

Program Impact:
This work has provided insights into the microscopic origins of macroscopic properties of heterogeneous polymers; hopefully, this will eventually lead to improved materials. The NMR techniques developed by our group have been and will be used worldwide by other NMR groups.

Interactions (External):
University of Southern Mississippi, Hattiesburg.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
John H. Dillon Medal of the Polymer Division of the American Physical Society (KSR '01). Total of 11 invited talks and 15 refereed publications in this topic area since 2003.

Personnel Commitments for FY2006 (Actual Effort):
K. Schmidt-Rohr (50%), A. Rawal (45%), E. Levin (50%)

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $270,000 **FY05 BA** $250,000 **FY06 BA** $245,000

Laboratory Name: Ames Laboratory
B&R Code: KC0203

FWP and/or possible subtask under FWP:
Materials Chemistry and Biomolecular Materials: 8. Bioinspired Materials: Aptamer-Mediated Templates for Hybrid Elastic Nanostructures

FWP Number: AL-90-360-001

Program Scope: Creation of a new class of biomimetic hybrid materials involving magnetite nanocrystals embedded in hierarchically self-assembling polymers. Controlling nanoscale magnetite synthesis using bacterial mineralization proteins and using DNA/RNA aptamers for achieving specificity of non-covalent binding within the polymer. Investigation of these novel materials and processes using experimental characterization tools as well as theoretical approaches combining modern polymer theory and the theory of micro-magnetism.

Major Program Achievements (over duration of support): We have successfully cloned the sequence for the bacterial mineralization protein mms6 from M. Magneticum and expressed it in E. Coli. Since most of the recombinant mms6 protein was insoluble and found in inclusion particles, the protein was renatured and successfully separated by affinity chromatography. Both the native as well as refolded mms6 proteins were found to facilitate formation of uniform cubo-octahedral nanocrystals of magnetite in solution with sizes of about 40 nm, as seen by transmission electron micrography. It is very difficult to synthesize nanocrystals with similar size and morphology by using other synthetic techniques. The magnetite nanocrystals obtained exhibited strong superparamagnetic behavior, which is typical for monodomain nanoparticles. In the presence of a self-assembling polymer gel, the formation of these magnetite nanocrystals was found to be much more controlled than in free solution. The nanocrystals formed in the presence of ferritin, another iron-binding protein as control, did not exhibit the uniform sizes and shapes seen in the presence of mms6. DNA and RNA aptamers are being developed to bind to mms6 as well as the self-assembling polymers. The approach was also used to synthesize cobalt ferrite nanocrystals in vitro using mms6 as a templating agent, because of their enhanced magnetic properties. Even though mms6 is not involved in the production of cobalt ferrite nanocrystals in Nature, the use of the mineralization protein was found to promote the formation of uniform cobalt ferrite nanocrystals in vitro, making it a truly general bioinspired approach for synthesis of uniform nanocrystals under ambient conditions.

Program Impact: The use of bacterial mineralization proteins to create uniform, monodisperse, monodomain nanocrystals of magnetite and cobalt ferrite in vitro represents a new paradigm for nanocrystal synthesis and processing using bioinspired methods. The non-covalent linkages and the hierarchical self-assembly processes enable bottom-up approaches for materials design.

Interactions:
Argonne National Laboratory

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
NSF-CAREER award (SKM, ‘00); MIT's Technology Review’s "Top 100 Young Innovators" list (SKM, ‘02); ISU College of Liberal Arts and Sciences Award for Excellence in Research Creativity (GAK, ’01); ISU University Professor (GAK, ’04); ISU Regents Faculty Excellence Award (GAK, ’04); Federated Laboratories Consortium Distinguished Service Award (GAK, ’05); MIT’s Technology Review “Top 100 Young Innovators” list -TR100 Award (BN, ’03); 3M Faculty Award (BN, ’03); Fellow of the American Physical Society (PCC ‘02); Divisional Associate Editor for Phys. Rev. Lett. (PCC ‘02); Fellow of AIMBE (SKM, ’06). 8 publications and 6 invited talks since 2004.

Personnel Commitments for FY2006 (Actual Effort):
S.K. Mallapragada (20%), M. Nilsen-Hamilton (20%), P. Palo (25%), J. Banerjee (15%), L. Wang (15%), G.A. Kraus (5%), T.-W. Guo (20%), B. Narasimhan (5%), T. Prozorov (25%), D. Bazylinski (5%), T. Williams (20%), P. Canfield (5%)

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $0 **FY05 BA** $225,000 **FY06 BA** $395,000